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May 1978

First Annual Conference On Advanced Pollution Control For the Metal Finishing Industry

PRESENTED AT:
DUTCH INN, LAKE BUENA VISTA, FL
JANUARY 17 - 19, 1978

Co-sponsored by:

- The American Electroplaters' Society
- The United States Environmental Protection Agency

Industrial Environmental Research Laboratory
Office of Research and Development
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Cincinnati, Ohio 45268

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Foreword

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

These proceedings cover the research papers and discussions of the "First Annual EPA/AES Conference on Advanced Pollution Control for the Metal Finishing Industry." The purpose of the conference was to inform industry on the range and scope of research efforts underway at IERL-Ci to solve the pressing pollution problems of the metal finishing industry. It is hoped that the content of the conference and the subsequent proceedings will stimulate industry action to reduce pollution by showing through government-sponsored research at IERL-Ci that viable control options are available. Further information on these projects and other metal finishing pollution research can be obtained from the Metals and Inorganic Chemicals Branch, IERL-Ci.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

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Introduction

The U. S. Environmental Protection Agency's Metals and Inorganic Chemicals Branch and the American Electroplaters' Society have jointly designed a three-day, broad-scoped conference. This conference, entitled "The First EPA/AES Annual Conference on Advanced Pollution Control for the Metal Finishing Industry," was held on January 17-19, 1978, at Lake Buena Vista, Florida. The conference's primary purpose was to develop a dialogue between various key members within EPA and the metal finishing industry. Focus was placed on the air, water, and solid waste aspects of pollution control for this industry. The proceedings from this conference are contained within this EPA publication.

The program of this first annual conference was broken into three distinct segments: regulatory, R&D, and an exchanging viewpoint segment. The primary purpose of the first segment was to provide all conference participants with a detailed understanding of EPA's current and future regulatory impacts on the metal finishing industry. Key EPA officials, representing the Effluent Guidelines Division (water), the Office of Air Quality Planning and Standards (air), the Office of Solid Waste (solid waste), and the Office of Toxic Substances (toxics), described the various legislation by which EPA prepares and promulgates regulations. Each speaker, in turn, provided the audience with the current status of air, water, solid waste, and toxic pollutant regulations, with special emphasis on their direct impact on the metal finishing industry. The second segment was divided into three areas: research and development addressing air pollution control, water pollution control, and solid waste pollution control. Various EPA- and industry-sponsored programs addressing these three media were presented to provide the audience with a better understanding of the significant research and development activities. The third segment, exchanging viewpoints, was conducted during an evening session. An EPA/industrial panel comprised of EPA officials and industry representatives opened the floor to a free discussion. The primary purpose of this third segment was for EPA to develop a clear understanding of the research needs considered by the industry to be most important. These research needs became evident during the open discussion between the audience and the panel.

This conference, having been attended by over 500 men and women interested in the air, water, and solid waste problems associated with the metal finishing industry, was considered by many to be a complete success. The primary purpose of the conference, to develop an open dialogue between industry and EPA, was achieved. The highest priority research needs of the industry were brought out during the three-day conference and solutions are jointly being sought by EPA and AES.

The proceedings of this conference have been published in order that the benefits gained from this first annual conference can be disseminated among as many people as possible who are interested in solving the intricate pollution problems associated with metal finishing. These proceedings contain the regulatory presentations made by the representatives of the four regulatory groups affecting the metal finishing industry, as well as the research and development presentations by various parties actively conducting research and development programs to solve these same multimedia problems.

The EPA and the AES hope that these proceedings are distributed as widely across the metal finishing industry as possible so that many parties involved in metal finishing can be made aware of the impacts of this conference.

George S. Thompson J

George S. Thompson, Jr.
Chief
Metals & Inorganic Chemicals Branch, EPA

J. Howard Schumacher

J. Howard Schumacher, Jr.
Executive Director
American Electroplaters' Society, Inc.

Conclusions of 1st Annual Conference

A survey of conference attendees showed that the most outstanding feature of the conference was the face-to-face interaction between the Industrial and the Environmental Protection Agency staffs in an atmosphere of jointly attacking the technical problems associated with providing full environmental protection —while maintaining the efficient use of limited technical and capital resources.

A consensus was reached that there are specific problems for which additional R&D can help provide relief:

1. The disposal of residues from wastewater treatment is a continuously growing problem. There is inadequate data to determine the field conditions under which the waste is actually hazardous. Engineering data suitable for designing safe disposal sites is almost non-existent, much more scientific and engineering effort should be focused in this area.
2. The accuracy and precision of the standard method for determining levels of cyanide amenable to chlorination are in doubt. This information could be important in determining if plants are meeting effluent standards. It was suggested that the AES work with EPA in quantifying the accuracy of this method in electroplating wastewater.
3. There is a need for the continual transfer of R&D results to the industry.

KEYNOTE ADDRESS

Stephan J. Gage[*]
Presented by Steven R. Reznek[**]

I realize that most of you probably think that all of EPA is dedicated primarily to the regulation of environmental pollutants. Actually, however, EPA is a mix of organizations with varied responsibilities. In my brief time today I would like to give you — without using organization charts, or hopefully, any bureaucratic terms — an idea of just what the EPA Office of R&D is trying to accomplish.

I hope to convince you that our efforts can be helpful to metal finishers as well as to the Nation. I would also like to enlist your help in assuring that our efforts are practical and useful.

To give you an idea of the overall EPA R&D program, we currently run a $250 million a year business. Our job within the Agency is "research, development and demonstration" — not "regulation or enforcement." While we are a separate organization within EPA — I report to the Administrator — the Office of Research and Development does however, support the basic regulatory mission of EPA. It does this by developing the scientific and technical knowledge and tools needed for protecting the environment in the most effective way, with as small an impact on the economy of the nation as is possible.

Although it is easy to say that we will develop scientific and technical information and methodologies, we all know that in real life we never are fully prepared but rather are forced to go forward with less than absolute certainty. There is no doubt that, under the very necessary pressures to expedite actions to control the more obvious and severe environmental problems, we have been forced, in many cases, to devise remedies without having all the tools needed for the most cost-effective solution. When this happens, both the regulators and the regulated are put in an awkward position where the nation's resources are not as wisely managed as they have been if all the scientific and technical information were available to the decision makers. In view of the large investment this country is making to improve the environment — it is the largest non-military expenditure in our history — it is important that every effort be made to assure that these resources will be well managed. This is part of our task in ORD.

The R&D activity is divided into several categories (Slide 1).

Scientific Basis for Assessment and Enforcement

The first item — developing the scientific basis for environmental criteria — is an essential task if the nation is to utilize its resources where they are most needed.

The major concern in establishing environmental criteria is, of course, health effects. Once a pollutant has been shown to have an adverse health or environmental effect, we must try to understand how it moves through and interacts in the physical environment so that it can be adequately controlled in the most effective manner. The basic question, "How much of Compound X will cause a degree of environmental or health harm?" must be answered.

Approximately half of our R&D budget is devoted to studies which we hope will lead to safe but not unnecessarily restrictive pollution control standards that can be applied at the appropriate point. This is a tremendously complex task. To derive optimum standards requires a thorough and sophisticated understanding of health, ecology and economy — a challenge which, in most cases, may actually be beyond our capabilities in the near term.

Therefore, to be safe, broad, general controls are being applied to the release of pollutants known to be harmful to health or environment. This has led to the practice of applying technology-based standards, that is pollution control regulations that are based on the demonstrated capability of technology to control pollutants rather than on a detailed understanding of the harm a particular pollutant can cause. I know that many industrial representatives feel that technology-based standards waste resources since they can result in overdesign in some instances — just as industrial facilities are sometimes overdesigned when there is less than a

SLIDE 1

R&D Activities

- The Scientific Basis for Environmental Criteria
- Measurement Methods for Assessment and Enforcement
- Technology Assessment
- Cost-Effective Pollution Control Technology Development

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[*] Stephan J. Gage, Acting Assistant Administrator
Office of Research & Development
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[**] Steven R. Reznek, Acting Deputy Assistant Administrator
Office of Energy Minerals and Industry
Office of Research and Development
U. S. Environmental Protection Agency

desirable amount of data available. As we develop a better base of scientific data on the behavior and effects of pollutants in the environment, then future control methods can be applied more selectively, while still providing adequate protection.

In essence, then, the studies aimed at obtaining a scientific basis for environmental criteria are an attempt to develop information that can eliminate overkill in regulations as well as require tighter regulations to protect public health where appropriate. These studies are pointing to more science and less speculation in environmental decision making.

Measurement Methods for Assessment and Enforcement

Unless you have the methods to measure the presence of pollutants in the environment, there is very little possibility that an adequate scientific understanding of environmental and health impacts will be obtained. In addition, it is important that in controlling pollutants, we must know the sensitivity and limits of detection of our measurement techniques.

As you will be hearing shortly, the recent emphasis on addressing the presence of the 129 "priority pollutants" in industrial wastewaters has given very real urgency to this aspect of our research program. Also, as many of you are aware, there is a strong need for less expensive analytical tools that will allow the required information to be obtained without placing an obvious analytical burden on those being regulated. All of these requirements are addressed by the second item of our responsibility list — the development of measurement methods for assessment and enforcement.

Once again, this is not a simple task; it forces EPA to the forefront in chemistry, physics, and statistical techniques. In the assessment of potential environmental damage, for example, not only must we detect the primary pollutant, but we must be prepared to measure its decomposition products — and all of this usually must be done in the presence of potential interfering compounds. Analytical work of this character is not routine.

Measurement methods used for enforcement, on the other hand, must often emphasize simplicity and low cost since such methods are typically performed in thousands of plants across the country. In addition, such relatively simple analytical techniques are required to give meaningful results in different types of wastewaters containing a variety of possible masking or interfering compounds. Air emissions, in addition to the analytical burden, place a very heavy demand on sampling technology. The accuracy and limits of detection associated with each method must be fully understood to avoid false indications of violations and to avoid missing dangerous amounts of pollutants.

Technology Assessment

One of the most important types of information needed for both a standard-setting and research and development program is a thorough knowledge of both the capabilities and cost of existing technologies when applied to impending problem areas. Unrealistic views of technology (either optimistic or pessimistic) either waste resources or miss opportunities. As the nation begins to rely on the widespread application of advanced technologies in the energy area, for example, a realistic understanding of these capabilities is essential. We are, therefore, placing great emphasis on technology assessment, in which the technological capabilities are evaluated by those thoroughly familiar with their projected application.

For example, the energy crisis is expected to bring changes to manufacturing processes, both in the fuels and, in some cases, the raw materials used. New energy technologies — some of which have potentially serious new environmental effects — will likely be introduced in the coming two decades. We are attempting to evaluate those problems while the technology is still in the pilot stage so that the hardware development progresses with environmental considerations fully in mind.

This type of evaluation leads to what we are calling "anticipatory research," which simply means that our goal is to improve our evaluation of R&D needs so that information is available when needed.

Eventually, we hope to reach the point where "panic" environmental situations — the so-called "pollutant of the month syndrome" — are minimized because we will have an improved knowledge of the capabilities and effects of the technologies we are using. As much as possible we want to avoid the cases where contradictory data leads opposing sides of an issue to cite studies leading to opposing conclusions. Unfortunately, we will probably never see these situations completely eliminated. It is impossible, or at least impractically expensive, to do the work required to anticipate all problems in *every* new technology in the development stage. We do hope to avoid the situation where environmental doubts begin to creep into the application of a technology after hundreds of millions of dollars have been committed to or spent on development. This is just good engineering sense. Once again, it requires a high level of technical competence and close attention to the detailed practical aspects of technology.

Cost-Effective Pollution Control Technology Development

Of course, even a complete and authoritative understanding of the science behind environmental standards, combined with perfect measurement methods, is not of much use unless something can be done to control the pollution. It is pollution control technology that finally cleans up the environment. In the eyes of the metal finisher, this is the major direct cost of environmental protection. I heard this thought put another way by an industrialist — "It's where EPA's costs stop and industry's begin." This is not exactly true, however, since we do have an interest in seeing that industry does have good, reliable technology that is as inexpensive as possible. As a matter of fact, about half of the entire R&D budget is related to assessing and developing control technology. EPA realizes that there are only so many resources available to the nation, and the less expensive the technology, the more widely it can be applied.

This conference is specifically designed to keep you informed of the results of the control technology development efforts in the metal finishing industry. The metal finishing industry, by the way, receives a significant portion of our industrial pollution control budget. As you will see, we are encouraging the development of technology that can be broadly applied at a reduced cost, either in capital or in energy.

I feel that we have become increasingly sophisticated in our analysis of pollution control technology because of our recent efforts to address the interrelationships of air, water, energy, and solid waste of each problem. In this respect we often use the term "multimedia," a term which you will hear quite often from EPA people in this conference. It is a sign that we are becoming much more sophisticated in our analyses.

We are also becoming more knowledgeable of the many manufacturing processes, because we recognize that reduction of pollution within the plant can be more beneficial than that accomplished by end-of-the-pipe controls. We also want to make sure that technologies developed under EPA sponsorship are compatible with established manufacturing practices. As any of you who are in R&D, or technology development, know very well, a new technology which requires major changes in manufacturing practices is very difficult to sell.

Budget and Resources

With this background, let us take a brief look at how EPA spends its R&D funds.

This next slide shows how our budget is divided. As you can see, it is split about half for technology and half for science. The science portion covers health effects, ecological effects, transport and fate of pollutants, and environmental monitoring.

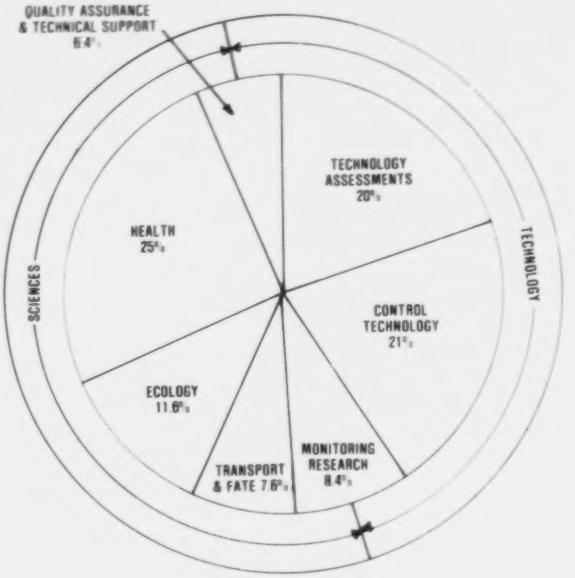
The next slide shows how we have divided our resources by category of problem. Energy-environment problems consume a large portion of our effort. Note also that there is a large interdisciplinary area.

Areas of Mutual Interest

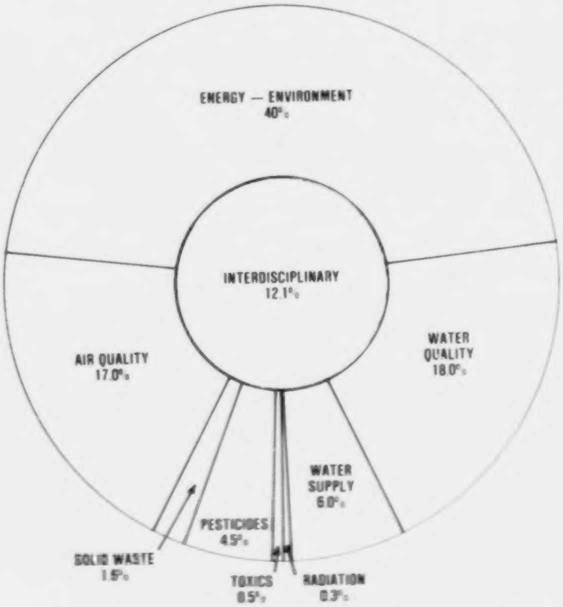
I hope that I have been able to give you at least a rough idea of what our R&D program is aiming for, and maybe, at least, have convinced you that we are not in an ivory tower — our goals are very practical and may be helpful to you.

Having seen this very quick view of our R&D program, a natural question might be, "Why should I cooperate with EPA R&D? It will just mean more regulations." Let us take these last few minutes and just explore the areas of mutual interest to see if we can answer this question.

SLIDE 2
Relative Ord Resource Allocation By Disciplines



SLIDE 3
Relative R&D Resource Allocations
By Category of Emphasis



I think that both EPA and industry have learned that standards and technology developed without an understanding of the practical aspects of the industry involved will lead to wasted technical and financial resources.

I think that originally many industry people thought that if the technological knowledge of the regulatory agency could be kept weak, it was more likely that weak standards would be applied. This just has not proven to be true.

What can really happen with inadequate technical knowledge is poor regulations that can have little beneficial effect on the problem and a repressive effect on industry. Good standards require a strong technology base, and this must be obtained by the technical people of both EPA and industry cooperating in the solution to environmental problems. That is why the EPA Office of R&D has assigned a significant portion of its budget for technology assessment, which must be done in cooperation with industry. That is why we have allocated funds to co-sponsor research for technology development with the American Electroplaters Society, the National Association of Metal Finishers and others in your industry. If we have good technology assessment data, we can understand your problems and work toward a solution.

In technology development, I know you are interested in meeting your environmental requirements at lower cost, with less energy use. We are interested in having you do just that, and we will work with you to prove out improved technology. We are looking for good projects for mutual cooperation. In this conference I hope all of you will make a personal effort to meet the EPA R&D staff for the metal finishing area.

Summarizing, then, I think that any reasonable person must recognize that there is a certain built-in conflict between the regulators and the regulatees — yet, on the other hand, we are all citizens of the same Nation trying to resolve problems in the most efficient way. It is not to anyone's benefit to see resources wasted. There is no group of people better qualified to devise the most efficient route to pollution control for the metal finishing industry than those who are in this room. We have formulated this conference as a first step toward making you aware of our R&D program and are inviting your present and future participation in it. We are very appreciative of the American Electroplaters' Society's effort in co-sponsoring the conference.

We hope that this is part of an increasingly cooperative attitude which will lead to more efficient technology and to better management of the nation's resources.

Future Water Pollution Control Regulations

Robert B. Schaeffer*

When we talk about the future water pollution control regulations, I am reminded of former Washington Redskins Coach, George Allen's famous saying, "the future is now." I want to talk today about what the Agency is about to do with regard to proposing pretreatment standards for the existing sources for the metal finishing industry.

For those of you who may not have heard the standard pitch, I would like to bring you up to speed with a bit of history. As Howard Schumacher was discussing, the 1972 Act, Public Law 92-500, identified the electroplating industry as one of the categories of industry for which we were specifically required to establish regulations. In March 1974 and again in April 1975 we did issue or propose some BPT and BAT regulations as well as some pretreatment regulations. BPT is our acronym for Best Practicable Control Technology, which was to be met for direct discharges into the Nation's waters by July 1, 1977. BAT, which is Best Available Technology Economically Achievable, is to be achieved by July 1, 1983, and the pretreatment requirements are to be met 3 years from promulgation.

Because of the controversy associated with those first regulations, the Agency withdrew them—actually withdrew part and suspended other parts—in December of 1976. The intent was to redo them, reassess the information available, and initiate an additional data collection effort. As a result of that effort, in July of 1977, the interim final pretreatment standards, covering a limited number of pollutants, were issued. These controlled cyanide, hexavalent chromium, and pH. These pretreatment regulations were in compliance with the Consent Decree, which perhaps you are aware of, that was signed in June of 1976.

The Agency signed this Consent Decree with some environmental groups to settle four different law suits that were brought against it. In the settlement, the Agency agreed to establish standards for toxic pollutants as defined under Section 307a of the Act. Now, these are different than the other toxics. So that you don't stay as confused as I am, we'll try to clear up the semantic problem. The Administrator has the authority to specifically identify pollutants without regard for the economic feasibility of the regulations. Under Section 307a, limitations may be established strictly on toxicity. Presently there are six of these regulations in existence which deal primarily with pesticides and PCB's. Another part of the Consent Agreement required the Agency to establish water quality criteria for 65 pollutants and classes of pollutants. The third lawsuit that was settled was for the Agency to promulgate pretreatment standards for eight industries—electroplating being one of those industries. The July 1976 interim final pretreatment regulations were issued to comply with the last part of the Consent Decree.

The regulations we'll talk about in a little while are an extension of that effort. There will be, however, a continuing review of the discharges of the 65 pollutants that I mentioned from the 21 industrial categories. You're lucky again in that you're specifically identified as one of those 21 categories. We will be reviewing the BAT regulations, new source performance standards, and pretreatment, which are to be reviewed and promulgated specifically looking at the 65 pollutants and classes of pollutants. These regulations will be issued by December 31, 1979.

Howard was talking about numbers: 21 or 65, and 128 and 129. We'll try to clear that up a little bit. The list of 65 pollutants includes a number of compounds, organic materials, specifically, that are identified as classes of compounds. In order for us to be very sure of what we're looking at, we sat down with our scientists, our analytical chemists, and the environmental groups and selected representative compounds from the list of 65. In fact, we expanded the list of 65 to 129. This includes 13 metals, 114 organics, cyanide, and asbestos.

In order to achieve the mission and the terms of the Consent Decree, we are undertaking four studies. We will continue to develop, with the assistance of our R&D program and you folks, technology-based discharge requirements. That is one of the studies that will be undertaken. We are just beginning that study. We have selected a contractor, one you're familiar with, Hamilton Standard, and they will be continuing to work with us in this area. The second study, which is very similar to what we've gone through in the past, will cover the economic impact and the costs of these technologies. We again will look to you for help in assessing, (1) the cost and, (2) what the impact might be.

The two other studies are a little bit different and are going to help us in making a final judgment. The first is the development of environmental criteria. Basically, I guess it's a matter of how bad these pollutants really are,

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*Robert B. Schaeffer, Director
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not only from a water standpoint but from an overall health standpoint. That will be the third study. The fourth I'd like to characterize as an environmental mass balance. How does the pollutant get into the environment? Where does it come from? Where is it manufactured? What products does it use? How does it get into the water? We will look at these other two studies and it will help us make a determination as to what level of technology is necessary to achieve the desired result.

Let me make an analogy. Suppose we were talking about regulating a pesticide and we had the choice between a 10-dollar technology and a million-dollar technology. When we looked at our criteria studies, we discovered that the pesticide was pretty bad and ought to be kept out. However, a look at our environmental mass balance study might reveal that if we imposed the million-dollar technology, we might only be solving 1 percent of the problem, because 99 percent of the problem would come from agricultural runoff. We hope to be able to apply both elements in making proper judgments when we go into our BAT review.

As a result of the proposal that was issued last July, we received many comments and have obtained additional data. Therefore, instead of going final, which is a normal progression in the establishment of regulations, we have decided to repropose the regulations and to open them up for an additional 60-day comment period. Hopefully, today, or within the next few days, the Administrator will sign this new proposed regulation and shortly thereafter it will appear in the Federal Register. Today, however, I will be able to tell you what it said when I left town. Until it is signed by the Administrator it is subject to change.

The numbers that appear on these slides, which include limitations for cyanide amenable to chlorination, hexavalent chromium, lead, and cadmium, will apply to discharges of less than 10,000 gpd. Many comments with regard to cyanide that we received after the proposal of the interim final regulations reveal that metals removal would have been required to achieve these cyanide levels. In reassessing our data base, we found that interdispersed in our numbers were some data points that were taken after clarification. Therefore, we went back and obtained additional data and reevaluated it.

This slide shows a daily maximum of 2 milligrams per liter and a 30-day average of 0.8 milligrams per liter for amenable cyanide. It also shows a hexavalent chromium daily maximum of 0.25 milligrams per liter, and a 30-day average of 0.09 milligrams per liter. The lead and cadmium numbers are ones; frankly, that we are not too satisfied with. We believe they ought to be more stringent. We will be looking very carefully at lead and cadmium in the next go-round. These numbers are based on the data that was available to us. Lead and cadmium, we believe, are particularly troublesome in the environment and we want to move toward maximum reduction of these materials. The numbers for lead are 0.8 for daily maximum, 0.4 for 30-day average; for cadmium, 1 and 0.5, respectively.

The cutoff point at a flow of 10,000 gpd was chosen to minimize the impact on the industry. In looking at the various levels with the high impacts that are forecasted, we chose this level in an attempt to minimize the impact on the most sensitive portion of the industry. The regulations are applicable to any firm that has an electroplating or metal finishing operation—captive shops, job shops—the same as has been in the past.

The next slide applies to all discharges greater than 10,000 gpd, but these numbers apply to all subcategories. There is a limitation left off for the precious metals; however. The only precious metal we are presently proposing to control is silver, and the number for silver for a daily maximum will be 1 milligram per liter, and the 30-day average will be 0.34. For plants discharging more than 10,000 gpd, we are adding limitations for total cyanide, total chrome, copper, nickel, and zinc. Lead and cadmium remain the same.

Let me try to explain total heavy metals. Many of you use more than one line, plate more than one metal. Our model technology, after precipitation, is solids removal. The metals, after proper application of this model technology, are contained mostly in the suspended solids that are discharged. If you are plating only one metal, the percentage of this metal in the suspended solids is significant. If you are plating a number of metals, the percentage of individual metals is reduced in the suspended solids. When you are talking about clarification, what you're trying to control is the suspended solids level. So we have included individual metals for those who plate only one metal. If you plate more than one metal, two number will apply. As you see, because of our data base and the application of our statistical analysis, some of them may not always add up to the total metal number, so the more stringent numbers will apply. Later on this week we can get into much more detail as to how this was derived and what we think it might mean to you.

Table 1 is a very quick run down of what the numbers are.

Table 1
Metal Limitations in Discharges From Electroplating Plants

Metal	*Daily Maximum*	*30-Day Average*
Amenable Cyanide	0.2	0.08
Total Cyanide	0.64	0.24
Hexavalent Chrome	0.25	0.09
Copper	4.6	2.0
Nickel	3.6	1.8
Total Chrome	4.2	1.6
Zinc	3.4	1.5
Lead	0.8	0.4
Cadmium	1.0	0.5
pH	No Limitations	
Silver	1.0	0.34
Total Metals	7.5	3.9

I do want to show you another option that we want to propose. We're doing this because of the dealings that you may have or may want to have with your local publicly owned treatment works. If a plant does not use strong chelating agents that inhibit the precipitation and removal of metals, if the plant uses lime as the neutralizing agent and removes solids, we have substituted a total suspended solids limitation for the common metals and the total metals limitations. The waste treatment plants are familiar with handling solids, measuring suspended solids, and understanding it, and we are proposing this approach in an attempt to reduce your monitoring costs.

We still are including limitations on lead, cadmium, cyanide, and hexavalent chromium, because cyanide and hexavalent chrome need to be handled before good metals removal can be achieved; and lead and cadmium again are of primary concern to us. We are limiting pH in this option from 7.5 to 10.0. In this option, the amenable cyanide, the total cyanide, hexavalent chromium, the lead, and the cadmium numbers are the same as stated for the earlier limitations. The only addition or substitution is a limitation of a daily maximum of 15 milligrams per liter of suspended solids and a 30-day average of 10 milligrams per liter of suspended solids, which was substituted for the copper, total chrome, nickel, and zinc limitations. You will notice that in this option we are specifying the technology to be employed and are presenting it as an option, if it is adopted, so that you can choose the approach for treatment that you wish to take.

The Agency has been very concerned over the high economic impact that is predicted in this area and on this industry. That is part of the reason that we're almost a year late with these standards and the reason we are reproposing them. Much work has been done to look for ways to mitigate this economic impact. The reason being, in addition to the concern over the impact, that these particular pollutants are also of great concern. The regulations that will be adopted will contain considerable verbage and they will discuss ways that the Agency seeks to mitigate the high impact.

There have been high-level Agency discussions between EPA and the Small Business Administration (SBA) to make their disaster loan program more accessible. The regulations will identify individuals in each of our regional offices who have the responsibility as the SBA coordinator. They will also identify the local individual in SBA who is responsible for their loan program in that geographical area.

We hope that we will be able to provide more such informational dissemination type seminars around the country to help folks at the local level through the red tape and paperwork that we're trying to minimize if the use of an SBA loan is appropriate. There are other means that we are looking at and that is part of the reason why we established, back last July, the interim final regulations for only a few of the pollutants. That is why we are reproposing again here and that is why there is up to 3 years for compliance. We are trying to phase this to minimize the impact.

We have found that this industry does not necessarily follow the same characteristics as all of the other industries in that the job shops, because of their size, are impacted the most, and the indebtedness of a particular company also can influence the impact. We would appreciate any thoughts that you have on further things that we might do to help along these lines.

With all that we've been talking about since 1972, from the outset there has been a general agreement between EPA and the industry associations as to what the applicable technology is. For some 5 years we have been discussing what that technology will produce in the way of effluent limitations. The numbers I have given you today reflect the data that we have available to us. There will still be some concern, I'm sure, and we will still be open to discussion on these particular numbers.

That pretty well covers where we are. I had thought and had hoped that I would have regulations in hand, enough for everybody, when I spoke here. I do apologize for the fact that we haven't processed them through the Agency as yet, but one good reason is the basic concern for putting out good regulations. I hope that our discussions over the next couple of days prove fruitful; and if there is anything that I or Dev Barnes, the project officer, can do to assist or give you information, we'd be happy to.

Future Air Pollution Control Regulations

Don R. Goodwin[*]

I was pleased when I was invited to participate in this work seminar and to discuss with you EPA's air pollution control program as it relates to the control of emissions from the coating of metals products. The core of the problem, as has been mentioned previously, is photochemical oxidants. The emissions from your industry — hydrocarbons — generally are not considered pollutants. It is what they become that brings the regulatory process to bear, because in the presence of sunlight, volatile organics react with other pollutants to form photochemical oxidants or smog, as we have come to know it. This smog is known to cause many adverse health effects. Among them the aggravation of heart and lung disease, particularly among the elderly, including aggravation of asthma, coughs, chest and eye irritation, and headaches.

An analysis of all the medical data in the late 1960's led EPA to promulgate an ambient air standard for oxidants in 1971. This standard is 0.8 parts per million for a maximum 1 hour concentration, not to be exceeded more than once per year. With this ambient standard came a need to curtail the release of hydrocarbons and other Volatile Organic Compounds (VOC), which are precursors of photo-chemical oxidants. In comparison to the current levels of oxidants in the atmosphere of our major cities, the national ambient standard is extremely tight.

Despite a major effort over the past few years to reduce VOC emissions from automobiles and stationary sources, most metropolitan areas of the country now experience oxidant levels well in excess of the national ambient standard. The standard, therefore, has led to a great deal of controversy in the past few years. There have been complaints by States and a consequent lack of action because they believe the standard to be unattainable with what they feel were reasonable regulations.

The industrial community has also suggested that the standard cannot be achieved and therefore must be relaxed. In addition, they have pointed to problems of natural backgrounds. In response to these allegations, EPA has conducted an extensive review of the standard and intends to announce the results of this review in March of 1978. The results could be a reaffirmation of the present standard or proposal of a less restrictive, or even a more restrictive standard. Preliminary information that I have seen does not show a justification for a major revision of the standard.

Since the original state implementation plans were submitted by the states, EPA and state agencies have been collecting ambient air network data. There is no doubt these regulations did not achieve the national health standard for some basic reasons. To name just a few:

- The regulations were not sufficiently restrictive.
- We did not understand the impact of reactivity and transport.
- Many sources were not identified in the regulations.

What the marketing also shows is that transportation related emissions have been dropping as automobile controls have been imposed, but stationary source emissions have not been reduced appreciably. At present, approximately half of the air quality control regions in the nation are exceeding the standard, in some cases by a factor of two or three. In addition, oxidants or oxidant precursors are being transported out of urban areas, with the result that the oxidant standards are being exceeded in rural areas almost as regularly as in urban areas.

Obviously, the strategies in effect were not sufficient and EPA, therefore, was required to direct a number of states to revise their state regulations. This situation was addressed by the Congress when they modified the Clean Air Act Amendments in August 1977. Under the revised Act, states are required to submit new plans for all non-attainment areas on January of 1979 — most metropolitan areas are presently classified as non-attainment for oxidant. The Act further requires that the revised state regulations be designed to achieve the ambient health standard by December 31, 1982. It further stipulates that if a state demonstrates that such attainment is not possible by 1982, despite implementation of all reasonably available measures, an extension may be granted, provided that compliance is achieved as expeditiously as practicable but not later than December 31, 1987.

It is in the area of all reasonably available controls that I am here today to discuss what the surface coating industry and other stationary sources will have to accomplish over the next few years to meet these anticipated state regulations. If we look at the first viewgraph we can see that VOC are released from a variety of stationary sources as well as motor vehicles. Approximately 17 million metric tons from stationary sources are principally traceable to the refining of petroleum, the manufacture of organic chemicals, the distribution of gasoline, waste combustion, and the evaporation of solvents. We note too that no single source category dominates the list; however, approximately 2.5 million tons or about 15 percent of stationary source emissions are generated from the application of industrial and architectural coatings and related operations.

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This next slide gives you an approximate breakdown of the thousand metric tons annual emissions from industrial surface coatings, in such industries as large appliances, magnetic wiring, automobiles, cans, coils, paper, fabrics, metal furniture, wood furniture, flat wood, miscellaneous metal products and the miscellaneous sources. It comes to about 2 million tons per year. Those are our approximate calculations of the impact of hydrocarbon emissions from industrial surface coatings.

The problem is extremely complex, and the technology to control sources such as your own is also very complex. EPA recognizes this problem, and in order to assist states in assessing this difficult area we have been assembling control technique guideline documents that review control technology and costs for almost all principal solvent emitting sources. To date we have released 10 documents covering sources of approximately 4 million tons per year VOC. The documents released are concerned with the petroleum industry, gasoline marketing, solvent degreasing, and surface coating. Additional documents are planned over the next year and a half for the remaining significant sources. We hope to cover most of the solvent coating industry by the end of 1978. Completed documents encompass surface coatings for automobiles, cans, coils, paper, fabric, magnetic wire, metal furniture, and large and small appliances.

This next slide is a brief rundown of what has been completed and what is in preparation for your industry for this year. The attempt here is to issue documents that discuss the technology, give some information on the cost and give the impact pro and con of the different types of control technology. These will be made available to the states, and it is their job to use this as a starting point to develop their regulations. The plan is to issue these documents to the states, and allow them one year in which to submit the regulations.

These control technology documents, which have been reviewed extensively in final draft stage by the industry and by environmental groups and state agencies, are concise, no-frills documents that review the processes that generate VOC as well as principal control alternatives and related costs and enforcement procedures. They do not represent regulations in themselves. But, they do give a perceptive, normal emission limit for most sources and as I said, are primarily designed to assist an energetic state technical person in understanding the technology on which to base his regulations. So far documents for the first five source categories have been completed and issued to the states, and regulations will be due under the state plans by December 31 of this year.

These control technology documents for surface coating generally express the emission limits in terms of solvent mass per unit volume of coating minus water. For example, the presumptive limit for top coating of automobiles is, under the new system, 0.34 kilograms per liter, or if you are old fashioned like I am, it is 2.8 pounds per gallon. The operator can meet this requirement by employing a powder coating, a high solids coating that contains no more than 2.8 pounds of solvent per gallon, or a typical waterborne coating of 26 percent solids. If the operator preferred, he could employ stack gas treatment to achieve the equivalent emission level. It is also a fact that these limits do represent VOC reductions of 65 to 90 percent compared to conventional coatings.

It is EPA's intent to specify these productive loadings but not to require any specific control technology so that the operator is free to choose his most cost effective approach to achieve the recommended level. Most installations will choose low solvent coatings, but some operators may choose incinerators or adsorption because of characteristics of their process. Some, of course, will employ innovative application techniques on air circulation possibly combined with stack gas treatment or coatings of their immediate solvent content. And what I have been outlining so far is an assistance program to state agencies which will, we hope, assist them in understanding the technology of your industry and give them some guidance. They have been pressing very hard for guidance for a long time to develop reasonable state regulations.

The second thing that happens is that we will take these same technology documents and increase the content considerably and turn them into what we call a standard support document; that is a technical document supportive of a national new source performance standard. That is under Section 111 of the Clean Air Act and is a regulation that applies only to newly constructed sources. This documentation is much more detailed, because the regulation must be based, to a large degree, on technology availability and on the cost. Under the new amendments, we also must give consideration to the environmental impact.

Six months ago we would have assumed that low solvent coatings would have been the choice to achieve these reduced emission levels. Low solvent coatings save sources energy and, by some predictions, save money for the operator. Generally, we are disappointed with the lack of acceptance of low solvent coatings method. We hear many reasons why powder or high solids or waterborne will not work for some specific applications. For example, powder coatings are not, so the auto industry reports, feasible for metallic paints. And 50 percent of our cars now have metallic paints. Also, powder coatings will not produce the necessary thin film and they are difficult to apply where frequent color changes are necessary. Waterbornes are alleged to cause costly paint line renovations, consume added energy, and are untried in many products. High solid coatings often cannot be formulated with sufficiently low level solids to satisfy the anticipated regulatory requirements.

The task we face in advising the states, with your help, is sorting out the difficult from the impossible. EPA, in spite of being able to hire some very qualified contractors and with some very qualified personnel in house, will not be able to match industry's expertise in paint formulation application. We are making much progress, however.

One large automobile company recently proposed to convert their entire industry to the equivalent of waterborne in 10 years. Now 10 years is a long time, but the program that they are proposing costs billions of dollars and that is a giant step.

In summary then, the guideline documents will focus on positive control of VOC and not substitution of compounds of lower reactivity as was the case with the Los Angeles Rule. The use of low solvent coatings is emphasized, since they can have a marked and quick effect on the VOC emissions. For example, an operator using 30 percent by volume solids could reduce the emissions by 60 percent by using coatings containing 50 percent solids. Even more dramatic reductions will be realized by the users of highly diluted coatings, such as lacquers. In this case, the operator now using 10 percent solid lacquer could achieve an 88 percent reduction in emissions by switching to the 50 percent solids enamel.

In the other two areas of control, that is incineration and carbon adsorption, the progress also has been very slow. Most of the incinerators in development today are aimed at high efficiencies and most use heat exchangers. Vendors report extremely high heat recoveries with concomitant minimal fuel inputs. In most instances, these designs come with higher capital costs than conventional incinerators, but promise substantial reductions in fuel. Design improvements are even slower with carbon adsorbers. The principal new innovation is a continuous unit in which carbon is pneumatically transferred from the adsorber to a stripping column. A few such units are now being installed in this country. We anticipate that adsorption will find increased usage, particularly in those areas where the recovered solvent can be reused in the process.

In conclusion, the solvent coating industry can expect an increase in pressures to reduce the atmospheric emissions of VOC. It is too early to tell whether industry's needs will be met by basic processes and coatings changes or by add-on, end-of-the-line hardware. In either case, the challenge is presented to the technical community to develop solutions rapidly in order to strike a balance between energy, economy, and the environment.

The EPA Solid Waste Management Program

John Dickinson*

I would like to do three things this morning. One, give you a brief overview of Resource Conservation and Recovery Act (RCRA); two, go specifically into hazardous waste, which I think you will be most interested in, and three, try to tell you specifically, how I think it is going to affect you.

As you might know, on October 21, 1976, the President signed the Resource Conservation and Recovery Act. This is really in update of the Solid Waste Act of 1965 and the Resource Recovery Act of 1970. The major objectives of this Act are to regulate hazardous waste, to make sure that non-hazardous waste is disposed of in an environmentally sound manner, to promote comprehensive solid waste planning, and to promote resource conservation and recovery; thus, the name.

I would like to look now at why the Resource Conservation and Recovery Act was needed. It was actually needed to complete the control loop. Substances removed from the air and water in many cases are going to the land, and there was no control of these hazardous residues. In addition, there has been considerable damage caused by this lack of control, so Congress wanted to close the loop.

I would like to look at the definition of solid waste that Congress gave us to work with. The term solid waste means any garbage; refuse; sludge from a waste treatment plant, water supply treatment plant, or air pollution control facility; and other discarded material, including solid, liquid, semi-solid, or contained gaseous material resulting from industrial, commercial, mining, and agriculture operations.

I would like to look at the term disposal, which means discharging, depositing, injecting, dumping, spilling, leaking, or placing of any solid waste or hazardous waste into or on any land or water so that this material may enter the environment. So it is a very comprehensive definition, a very comprehensive Act.

First, I would like to look at non-hazardous waste for a moment. Assume that your waste is not hazardous. What happens to it? Well, EPA is maintaining indirect control through State plans. For hazardous waste, EPA is in direct control. The key is to work with the State Directors and develop a State Plan. This is a very weak enforcement plan for non-hazardous waste. Mainly, what we do is define what a sanitary landfill is. (These criteria are out in draft form now, and they are to be promulgated shortly.) Everything that does not fit the definition of a sanitary landfill is an open dump, and they are illegal. The State Plan must show how these open dumps are going to be closed. The municipalities or person operating an open dump can obtain a compliance schedule up to 5 years to either up-grade an open dump or close it.

One of the first things EPA is required to do is develop an inventory of all open dumps. With the way solid waste is defined, you can imagine how difficult this will be, because this includes industrial impoundments, lagoons, anywhere you dispose of solid waste.

Our first priority is to develop a municipal open dump inventory by working with the States. Thus this will not affect industry right away. Possibly, in the future EPA's safe drinking water people will do an industrial impoundment assessment, so we feel that the industrial part of the inventory will be sometime in the future. So, if your community were operating an open dump, it would go on this inventory and be published in the Federal Register with a compliance schedule.

Now we feel that by closing these cheap open dumps we will promote resource conservation recovery. In addition to closing open dumps, we have resource recovery panels, which will be used for doing a lot of studies. These studies will cover plastics, sludge, and such similar things. We are also going to require the States that receive our money to buy a maximum amount of recycled material. In short, we are closing the open dump and we are trying to improve the market for secondary materials. We also are going to try to make the information available to the public, because we feel as though public education is one of the big things in municipal solid waste and recycling.

Now let's look at hazardous waste. Section 3001 of Sub-title C answers the question of what is a hazardous waste. The way EPA will apply this is in utilizing criteria and lists, such as flammability, corrosiveness, radioactivity, biochemical activity, and carcinogenicity. We have a whole list of things that are bad.

There are two bad aspects: one is transporting hazardous waste to the disposal site; second, after you get them to the disposal site, what happens to them? You will be concerned with both of these, since you might be treating or disposing on site. So the first thing you do is determine if your waste is hazardous. EPA has agreed to help your industry on this, and we have said, based on our knowledge of the criteria, we feel like water treatment

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sludge (and this is not in the promulgated Federal Register, this is just in the draft stage) from the electroplating industry is hazardous, based on its toxicity. If you want to be removed from the list of those disposing of hazardous waste, you must go through toxicity tests and show us that your waste is not toxic. That is the way the regulations are headed right now.

If you have hazardous waste, what do you have to do? For one thing, if you generate hazardous waste you do not need a permit. The Congress specifically did not want generators to need to obtain a permit. But once you generate hazardous waste, then Congress wants us to work with you to make sure it is properly handled. So, the next set of regulations will be Section 3002, which will be generator standards. This basically says that you have to fill out a manifest if you want to ship your waste off site. This manifest is given to the transporter, who takes it to a facility with a permit to store hazardous waste. A copy of the manifest is returned to you stating that the waste has been received. Then you report to EPA each quarter that there are no disposal problems. But, you must supply a list of all the loads of waste and where they went. That list is compared to a list supplied by the disposal man. If you store for over 90 days, you must obtain a storage permit. If you dispose on site, you must obtain a disposal permit. But we are allowing industry 90 days to accumulate an economic load of waste before a permit is necessary, but you will still have to fill out the manifest.

The next set of regulations will cover transporters. Although this is of little interest to you, I will cover it briefly. It says the transporter must follow DOT regulations; he must take the manifest, sign that he has received a load; ship it according to DOT regulations; and assure that it reaches only a permitted hazardous waste treatment storage or disposal facility.

Let me return to the criteria for a moment. The main thing you will be interested in is the toxicological properties of your waste. Is it toxic?

The next important part is the standards. If you decide to treat or dispose on site, the next regulations say, basically, you must protect the air, ground water, and the surface water. (This is the first draft of Section 3004, Draft Regulations.) It says that you have to collect all water from your disposal site, you must obtain a NPDES permit, and you must insure that no contaminants get to the ground water. It is written so that there is no degradation of the ground water, no endangerment, this is a technical term. I won't get too deeply into that, but there are specific standards that you must meet if you want to treat, store, or dispose on site, and these standards have been issued. You can obtain a copy of these if you want or you can work through the society.

Section 3005 of the Act describes how to obtain a permit. Basically it says that you must meet these standards and it provides all the details on getting that permit; it is like all your other permits, you have to go essentially to the same steps to get your permits.

An important part of the Act to metal finishers might be Section 3006 that deals with State programs. It says — and it's EPA"s intent — to let the States run the hazardous waste program if they are equivalent to the Federal program. They can be more stringent, but not less stringent. The Act lets EPA give a state interim authorization for up to 2 years in which time they must bring their program up to Federal standards. So it has been EPA's conviction that the State can do a better job of running a hazardous waste program as long as they meet national standards that apply to everyone. So, Section 3006 will be encouraging States to run waste programs.

Finally, you might ask, what is the first thing I've got to do under this Act? The first step comes under notification. What EPA will do is mail you a letter saying we have reason to suspect that you have hazardous waste and this is to help you notify us. You can fill in the blanks — a very brief form — and send it back to us. Unless you notify us, you cannot treat, store, or dispose of hazardous waste. So it is very important that you notify EPA that you have hazardous waste that you are generating, transporting, treating, storing or disposing of. When is that going to be? Our regulations were due, all of them, in April 1978. It looks like it's going to be summer or possibly fall before some of these get out. So late this year or early next year, you will receive this letter.

We have talked about Sub-title C regulations, and as we've tried to indicate where it will affect you and how it will affect you. I know you don't want to have a hazardous waste, but in order to get off EPA's list, you will actually have to test.

Thank you.

EPA Activities Under The Toxic Substances Control Act

John B. Ritch, Jr.*

The Toxic Substances Control Act is now a little over a year old — yet, thus far little direct effect has been felt. In fact, from my vantage point it appears that many persons and firms which deal with chemical substances are just now learning of the Act's existence and the breadth of its eventual impact. However, on January 1, 1977, when this Act became effective, a whole new perspective for the chemical industry was launched.

We live in a world of chemicals — in the clothes we wear, in the food we eat, in the air we breathe. It is estimated that there are between two and three million known chemical compounds with some 30-40,000 in commercial production. Several thousand new ones are discovered each year and several hundred of these channel into commercial use. Obviously this means that much of our technical skill is devoted to finding and developing new chemical substances to afford us a higher standard of living. It has been this way for many years. So why have we suddenly become concerned about chemical substances?

In reality, this is not a sudden concern. Just as our technology has advanced in the plastics field, the elastomer field, and the plating field, so has our technology advanced in the pathology field. Over a long period we have been learning that while there are great benefits to be derived from the uses of these substances, some of the substances also pose severe health risks. Several studies, especially in the last two decades, have equated chemical substances with both immediate and long-term health dangers, as well as severe ecological damages. These equations led to the regulation of radiation in the 1950's, followed by further environmental legislation dealing with air and water pollution, pesticides, and solid waste disposal. All of these regulatory actions deal in some degree with the control of certain chemical substances which might create either human health or ecological problems. Yet, Congress felt it necessary to enact TSCA. One could say this closed a loop.

TSCA came about because there are significant differences between the environmental contaminants that have been the focus of air and water pollution control efforts and the ones that have more recently been in the headlines—PCBs, PBBs, vinly chloride, kepone, chloroflurocarbons, and others.

Take air pollution control, for example. Through most of the 40 to 50 years that any real effort has been made to reduce air pollution, that effort has been focused on pollutants, such as particulate matter, carbon monoxide, sulfur dioxide, and nitrogen oxides. These pollutants are by-products, entering the environment entirely through tailpipes and smokestacks.

Now, take one of the substances recently in the headlines—polychlorinated biphenyls-PCBs. These are not by-products of combustion or industrial processes. They are commercial chemicals. They have been produced, distributed, sold, used, and discarded, not only as bulk chemicals but principally in many industrial and consumer products, such as transformers, capacitators, and condensers. Though steps are taken to control PCB discharges during manufacturing and processing, these have not been sufficient to prevent PCBs from contaminating the environment and endangering human health. The discarded items alone have put PCBs in drinking water systems and have contaminated lakes and streams and the attendant fish. Congress felt so strongly about protecting us and future generations of Americans from the hazards of PCBs that they put a special section in TSCA to ban the future production and distribution of PCBs. Since there *may* be other substances out there with hazards equally as great as those we have accidently learned about, Congress has said—thru this Act—let's find out about these chemical substances before they hit the environment—instead of after-the-fact.

It is not the intent of TSCA that EPA ban the production and distribution of all commercial chemicals. Far from it. The Agency does have the power from the Act to prohibit the production and use of chemicals, if found necessary, but it also has many other ways of attacking toxic substances problems. One of the major thrusts of TSCA is to create and maintain a knowledge base, which will enable preventive, rather than reactive, positions on any chemical substances determined to be hazardous. To be able to mount an effective attack on toxic substances problems, the EPA needs to be able to determine which chemicals pose truly significant problems, how those chemicals affect human health and environmental quality, how they reach the environment, how great a risk they pose, and how to deal with them without creating even greater threats. What we are now setting about to do is to learn about the chemicals through thoughtful study—not as we have—

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unfortunately—so many times in the past—through accidents.

In specific terms, TSCA authorizes the Environmental Protection Agency to (1) obtain information about existing and new chemicals and to take appropriate action against those which represent unreasonable risks; (2) require that manufacturers and processors of potentially harmful chemicals conduct tests and submit to EPA data on the effects and the behavior of these chemicals; (3) require that EPA be notified in advance of the manufacture of new chemicals and supplied with information necessary to evaluate the effects of these new chemicals on human health and the environment; and (4) when necessary, take steps to limit the manufacturing, processing, distribution, use, or disposal of a chemical substance which may present an unreasonable risk. Now let's state this another way.

First, we must identify the existing chemical substances presently being manufactured or imported. This gives us a baseline for determining new chemicals.

Second, we must identify whether any existing or old chemicals may present any unreasonable risk, and we must establish testing requirements to confirm or disprove our concern.

Third, we must establish ground rules for determining whether a new chemical substance may pose adverse effects before it goes into manufacture, and lastly, we must have a sound program for taking regulatory action when a substance presents an unreasonable risk. What the whole Act really says can be put into two major parts: (1) let's find out what chemicals are already on the market—and are any of them hazardous? and (2) let's take a look at new chemicals before they get out in the marketplace. Let's be sure they do not pose any unreasonable risk. And, note that I said unreasonable risk—I did not say NO risk.

Our first step has been to turn to the task of determining the substances produced or manufactured in or imported into the United States. The Act mandated that such an inventory be made. This date has already passed and we do not have an inventory.

It would seem a fairly simple task to identify and list chemical substances. The law has provided some exemptions, such as pesticides, foods, food additives, drugs, cosmetics, firearms and ammunition, tobacco products, and nuclear materials. But, how do you treat mixtures, such as paint? Should we list all the innumerable polymeric combinations that are developed for adhesives, rubber, plastics, etc.? How about alloys and plating? The task is not quite so simple. There must be acceptable resolutions to these issues.

One of the best ways to seek resolution is to seek the opinions of both those the law seeks to protect and those whom the law seeks to regulate. So, one of our first actions was to consult industry, environmentalists, laymen, elected officials, and private citizens—in both public and private meetings—to bring together all their views. By doing this, we feel we can come up with what we believe to be effective and fair, reasonable and responsive rulemaking procedures.

After several weeks of intensive effort on this task, the Agency issued on March 9 the proposed regulations for reporting the manufacture and importation of chemical substances for the inventory. We also, based on our consultations, defined the types of substances to be reported and those that were exempt, such as chemicals for research and mixtures. Primarily, we sought only to determine the chemical identity of those chemicals manufactured.

The weight of the certain comments following our March 9 proposal convinced Administrator Costle that our proposed regulations should be revised. Thus, the reporting requirements were reproposed in the *Federal Register* on August 2nd. In addition to reporting chemical identity of substances manufactured or imported, the proposal required the site of manufacture, the volume of manufacture, and whether the material produced was used only at the site. The August 2nd proposal also offered a definition of "small manufacturer" who, for the purpose of this particular reporting, would be exempt from reporting *volume of* production. The requirement for reporting of imports was modified so that only chemical substances imported in bulk must be reported.

After the August 2 reproposal another period for comment was allowed, which ended September 16. We then became engaged in evaluating the comments received earlier together with the new comments in an effort to arrive at the final reporting regulations. This development, of course, upset the schedule set in the Act. The final reporting regulations, together with the appropriate reporting forms, were published in the *Federal Register* December 23rd, with a reporting period of 120 days beginning January 1 and ending May 1, 1978.

After this four-month reporting period ends May 1, 1978, the Agency will amalgamate the information from the reports to come up with the inventory. This inventory, which we expect to be available in the fall of 1978, will contain the *chemical identity* of all the chemical substances reported to EPA as being manufactured or imported. It will also contain an Appendix of voluntarily reported trade mark listings. It will *not* contain the names of the producers or importers *nor* will it contain quantities. That information will remain within EPA. Here I want to assure you that EPA is well aware of manufacturers' concerns regarding confidentiality. EPA has established a task force to develop procedures to safeguard proprietary information from both inside and outside sources and will hold a public meeting soon to receive comments on its proposed procedures.

Although many persons have been concerned about the inventory, you should know that the inventory has no special significance as regards the hazard of the chemicals listed. No characteristics of any chemicals are asked for and none will be given; no categorization of hazard can in any way be attached to the list. We are only seeking to know precisely what substances, as such, are in fact being made and where, and how much. That's all.

The real significance of the final inventory is that it becomes the baseline between the old or existing chemicals and any newly developed chemicals. It means that any chemical substance not appearing on this inventory becomes illegal for use 30 days after its publication. It also means that all substances produced for commerce after publication of the inventory and *not* appearing on that list will be subject to obtaining premanufacturing approval. Just to make sure we have everything on the inventory, we are allowing a 210-day reporting period, a grace period, following the inventory's publication, for processors and users of chemical substances, such as yourselves, to verify that the substances they purchase appear on the inventory. If they do not, the processor or user, during this 7 month period, may report them and they will be added. It now appears that it will take us about 8 months after the reporting to compile the inventory—so it now looks like January 1979 before the initial inventory is published.

Let's consider for a moment how inventory reporting affects you. If your firm manufactures any of the chemical substances used in the paint or coatings business, it must consider its responsibility to report. I say consider, because it may not *have* to report if the manufacture of the substances is only a relative small part of its business. It *may* report to insure that the substance is on the inventory. Chemical substances purchased from other firms are not your responsibility. They should be reported by the manufacturing firm. Last but not least, although there may be a chemical reaction after the application of the paints or coatings, these are considered end products in articles and do not have to be reported. The substances included in the products have to be reported—but, as mentioned, most of these are probably purchased. Also, paints or coatings themselves as mixtures do not have to be reported.

When the inventory is published in January 1979, then, as processors, your firms should review it to see that the substances used are listed.

Now let's go back. The second phase of our strategy is to identify those substances which may pose a risk and develop the requirements for testing them to confirm or disprove the risk. To start this process, EPA organized in February an Interagency Testing Committee composed of scientists from eight government agencies. This Committee was charged with the responsibility for developing a prioritized list of substances recommended for further testing and reasons for inclusion of each substance or mixture on the list. The law directs that up to 50 of the listed substances or mixtures can be designated by the Testing Committee for priority testing. The Committee is directed by the Act to give priority attention to known or suspected carcinogens, mutagens, and teratogens in developing its recommendations which may be listed as individual substances or classes of chemicals.

The Committee's first effort was in the successive screening of about 3,000 chemical substances which had previously appeared on various hit lists. In July the Committee published a Preliminary List of 330 substances and categories of substances selected primarily on the basis of potential for human exposure and environmental release. The Committee, on October 4th, submitted its first report to the Administrator listing four individual substances and six categories of substances for consideration for EPA's priority review, with recommendations for the kinds of testing recommended. The entire text of the Committee's initial report, outlining the process and the basis of its decisions, was published in the *Federal Register* on October 12, 1977.

Now that EPA has this report, it is required by the Act that the Administrator initiate a rulemaking procedure with respect to each substance or category, or publish in the *Federal Register* his reasons for not initiating such a proceeding. It should be pointed out here that initiation of a rule on a substance is not a regulatory action. It does not ban the chemical nor limit its uses.

Rulemaking on a substance requires the manufacturers and processors of that substance to conduct such testing as necessary to develop health and environmental effects data. Testing must be relevant to a determination that there is *or is not* an unreasonable risk of injury to health or the environment by the chemical substance in its manufacture, distribution in commerce, processing, use, or disposal. In his decisionmaking, the Administrator, before requiring testing, must find that (1) the chemical may present an unreasonable risk; (2) there are insufficient data for determining or predicting the effects; and (3) testing is necessary to develop these data.

In substance, what the Committee has said is, Here are ten substances that may present an unreasonable risk. However, at this point, we do not know whether there are sufficient data to determine the effects. Therefore, the Administrator should make this determination and rule for testing if necessary. The Agency is now holding meetings with industry, associations, and environmental group representatives to develop procedures for requesting any health and safety studies that may exist on the substances named by the Committee.

Among the requirements that EPA must lay out are the standards for the development of the test data. This is an area where several work groups are now busily engaged. Much work must be done to determine and standardize the test procedures and regulations. It should also be pointed out that whenever a rulemaking on a substance is developed it will also specify the time period for developing the test information. In determining the standards and period to be included in a rule, our considerations must include the relative costs of the tests and the foreseeable availability of facilities and personnel to do the required testing. Thus, it may be seen, that with rulemaking and a long test program, any regulatory action on even the priority chemicals may be quite some time away.

The third phase in our program involves consideration of the risk of new chemicals before marketing. Thirty days following publication of the Inventory List, all new chemical substances—meaning those which do not appear on the Inventory, whether they are new or not—

and "significant" new uses of chemical substances, will be subject to TSCA's "premanufacturing notification."

This will be a screening through which chemical substances must pass before their initiation onto the Inventory List of existing chemical substances which can be legally marketed in the United States. By the end of next year, manufacturers of new chemicals will be required to notify the Administrator 90 days before manufacturing.

Here again, we're in the process of planning our testing procedures and regulations. If we are to carry out the mandate of the Act that our regulations are not to stymie technological innovation, our task becomes most difficult for we must try to find the way to obtain sufficient data to provide confidence that a substance may be approved for the marketplace while not requiring so much data that the costs will impede research and development of new substances. This is a tough assignment. And we're very much aware of it. Within the next six months EPA expects to propose rules on how we intend to handle this difficult issue. We are considering using hierarchical testing schemes. After first reviewing the physical and chemical properties of chemicals, under a suggested hierarchical method, they would be subjected to biologic activity testing which would involve relatively quick and inexpensive tests. Testing for prechronic toxicology would follow for high volume and high risk subclasses. Long term bioassay tests involving more expensive studies would follow in accordance with lengthier detailed test protocols to be approved by EPA.

That brings me to the question of what EPA is empowered to do under the TSCA when problems are identified. Probably the best known new authority that the Agency has under the Act is the power to ban or restrict the introduction of new chemicals and significant new uses. There are, or course, many interesting and important aspects to the premanufacturing review process. I will mention just two. One is the fact that the Agency is *not* empowered to register chemicals or license particular uses. The Act gives EPA a limited time in which to review information on new chemicals and significant new uses; if the Agency fails to take action within that time—action either to require the submittal of additional information or to propose a restriction—then the manufacturer or processor can go ahead and manufacture the new chemical. A second point worth mentioning is implied in what I have already said. EPA is not compelled to make an up-or-down decision on each new chemical or significant new use. As appropriate, the Agency can impose a variety of limitations tailored to prevent unreasonable risks and still permit potential benefits to be realized. For example, limited uses or special labeling.

EPA's authority to prohibit or restrict also applies to commercial chemicals already in use. The Agency can prohibit or restrict the manufacture, processing, distribution, use, and disposal of commercial chemicals. Again, the Agency's action can be tailored to deal with the particular activity that is causing an unreasonable risk. This authority is already being used, not only with respect to PCBs, for which the Act prescribed the action to be taken, but also with respect to chlorofluorcarbons.

One thing I believe all of us can extract from what I have related. This is, that the task of properly regulating and controlling chemicals to prevent hazard is a complex one. There are major issues to be decided—such as what is meant by "substantial risk"? How much data must the Agency require for premanufacturing approval to insure reasonable acceptance? Will this requirement not only tax the laboratory capability but stymie technology and new products?

We must also work to reduce the overlap of regulation between agencies. The Act has taken this into account and has directed the Administrator to integrate our actions with those of other agencies. Primarily, we must organize to make better use between agencies of the data that have been and are being submitted. We are working hard in this area.

Just a few weeks ago, Administrator Costle announced that EPA, the Food and Drug Administration, the Occupational Safety and Health Administration, and the Consumer Product Safety Commission have pledged to work together to develop compatible testing standards, common approaches to risk assessment, coordinated information systems, and, among other things, coordinated rulemaking and enforcement activities, research planning, and communication with the public. This unprecedented enterprise is aimed at better administration of Federal laws dealing with toxic substances. Thus, it should build upon and improve EPA's ability to deal with such problems under the Toxic Substances Control Act.

There is no doubt that the implementation of TSCA will sometimes be painful—both for the Environmental Protection Agency and the chemical industry. Some very difficult choices will have to be made. Whether our sons and daughters will have similar hazards to face 20 or 30 years from now depends on how effectively we implement and administer TSCA now. And that—in turn—depends upon how well the Environmental Protection Agency, the chemical industry—and that's many of you here today—and every other group interested in these problems work together to responsibly deal with them.

Overview of the EPA Research & Development Program For Air Pollution Control in the Metal Finishing Industry

Charles H. Darvin*

INTRODUCTION

The air pollution problems in the metal finishing industry come from a number of metal finishing industrial processes. No one industry within this category can be singled out as the only generator of air pollution. Specific industries, however, which are addressed by IERL-Cincinnati Research & Development program include the can and coil coating industry, the automobile industry, the machinery and appliance manufacturing industry and the general category of transportation sources. The major pollutant problem that is typical for all segments of the metal finishing industry is considered to be organic emission. Whether the organic material is found in the metal coating, paint, or used in metal cleaning or machining, it is generally emitted to the atmosphere. The most common air pollutant is the volatile organic solvent. Many of these are toxic in nature at worst, or at the least add to the national ambient air oxident problem. The scope of the research program in this area, although limited, is designed specifically to attack organic emission problems from metal finishing operations. The goals of this program are first, to develop or identify new or improved coating systems; or where necessary to develop or improve emissions control technology. Primary emphasis in the present program is to reduce emissions from metal painting and cleaning operations.

Air Pollution Overview

The metal finishing and fabrication industrial category is defined to include a variety of metal preparation, fabrication and coating processes. Industries in this category include, but are not limited to, automobile manufacturing and painting, shipbuilding, transportation equipment manufacturing, can and coil coating and appliance manufacturing. This naturally also includes metal fabrication and plating job shops which by the nature of the processes used produce some air pollution.

The air pollution research effort for FY 77 and FY 78 will result in the expenditure of approximately $300,000. Although limited, it represents a 350% increase for this industry over expenditures prior to 1977. This increase has come about through the realization that part of our national air pollution problems is due to emissions from various metal finishing and fabrication operations.

In prioritizing the air pollution emissions from the metal finishing industry for the expenditure of limited Research & Development air funds, the most pressing problem has been determined to be the release of volatile organic solvents to the atmosphere. These pollutants are at worst toxic or at the very least contributing factors to photochemical oxidant levels in the atmosphere.

The major sources of volatile organic pollutants from industry include industries such as can and coil coating, automobile painting, architectural painting and degreasing processes such as can be found in many job shops. The total nationwide emissions of organic pollutants is estimated by EPA to be about 28 million metric tons (31 million tons) of which 17 million metric tons (19 million tons) are emitted from stationary industrial sources.[1] Seven and one-half million metric tons are released from industrial processes classified as metal finishing processes.[1] These emissions, therefore, are considered to place a significant burden upon the nation's ambient oxidant level and health related impacts. Thus, recognizing the problems associated with organic pollutant emissions, IERL and MICB have placed the major emphasis of their air research and development programming on the control of organic emission.

In addressing the air pollution problem of the metal finishing industry and volatile organic emissions, in particular, a research and development program has been designed to encompass a variety of pollution control approaches. The general approach of the program is to develop viable low-polluting options to present production procedures and materials procedures and where process or material changes are not feasible to develop cost effective control technologies. Figure 1 outlines the general approach of this program.

Coating Technology Development

The basic fact underlying organic emissions to the atmosphere from painting and cleaning operations in the metal finishing industry is that eventually all of the solvent in the coating material will evaporate. Thus, a logical approach to eliminate this aspect of coating applications is the reduction or elimination of solvent-based coatings. Unfortunately, there is no universal coating or a

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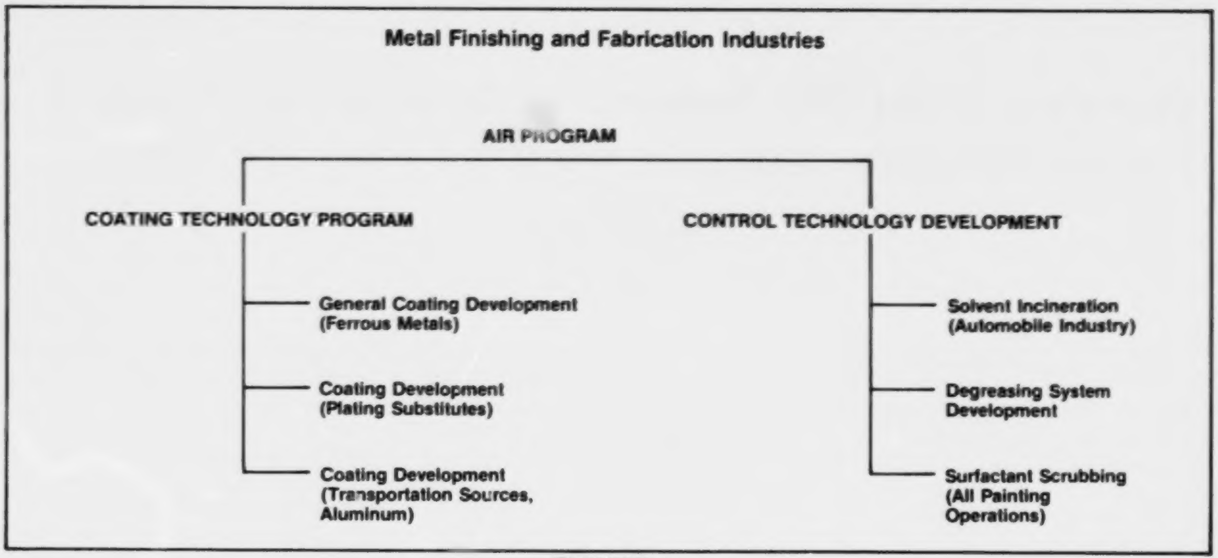
Metal Finishing and Fabrication Industries
AIR PROGRAM
COATING TECHNOLOGY PROGRAM
CONTROL TECHNOLOGY DEVELOPMENT
General Coating Development (Ferrous Metals)
Coating Development (Plating Substitutes)
Coating Development (Transportation Sources, Aluminum)
Solvent Incineration (Automobile Industry)
Degreasing System Development
Surfactant Scrubbing (All Painting Operations)

FIGURE 1

small group of coatings which will serve all product requirements. Coatings are product specific and are formulated for specific product and product requirements. Thus, there are an infinite number of coating formulations. Added to limitation on coatings is the requirement for extensive testing for new coatings before customer acceptance.

Recognizing that it is impossible to develop coatings for each specific requirement, the coating development program primarily is limited to programs that have immediate payoff to industry and their use can be used by more than one source. Highlighted in this coating development program is the PACE program. This grant program with the Steel Structures Painting Council will evaluate new and generic coating developments. It is designed to screen new coatings and evaluate their potential to reduce pollution while maintaining or exceeding present product standards. This program should have and is having a major impact on identifying new coating systems that will reduce pollutant discharge to the atmosphere.

A second and more limited program cosponsored by IERL-Cincinnati is being carried out with the USAF. The goal of this program is the development of a high solids, high quality coating technology for use on aircraft. Although, presently directed only toward military aircraft, the developed coating will have potential applicability to commercial aircraft painting as well as other transportation services such as railroad cars and heavy construction machinery. The resulting coating system will have applicability on both aluminum and steel substrate.

A third research project which is directed at both air and water pollution is with the Grumman Aerospace Company. This program is investigating various low-polluting coating systems for application as a potential coating to machined parts as would be produced by small job shops. Some of the output of this project is presently being tested and utilized by a number of companies.

Emissions Control Technology Development

Since new coating systems cannot be developed in a timely fashion for all coating applications, we also have incorporated into our R&D program as a parallel avenue activities directed toward control technology research and development. Projects in this area are designed to develop and demonstrate potentially viable control technology concepts that will capture, contain or destroy organic emissions. Highlight programs in this area include a major testing and evaluation program of shop size vapor degreasing systems.

This study will evaluate state of the art technology for reducing and containing degreasing solvent emissions. Various degreasing system design features will be evaluated to determine their efficiency in reducing solvent emissions while in operation. This project will serve as a guide to EPA and industry on the types of development actions needed to reduce organic pollutant emissions from degreasing operations and simultaneously define emissions and operating characteristics of these systems.

A second major program in this area is directed at automobile manufacturing. New design concepts in auto paint baking ovens may permit reduction of emissions while significantly reducing the oven's energy consumption. In cooperation with a major automobile manufacturer, EPA is presently conducting an evaluation of a paint bake oven system designed for this purpose. The results of the evaluation will verify the feasibility of incineration of solvent-laden oven emissions from large-scale zoned operations. This project can

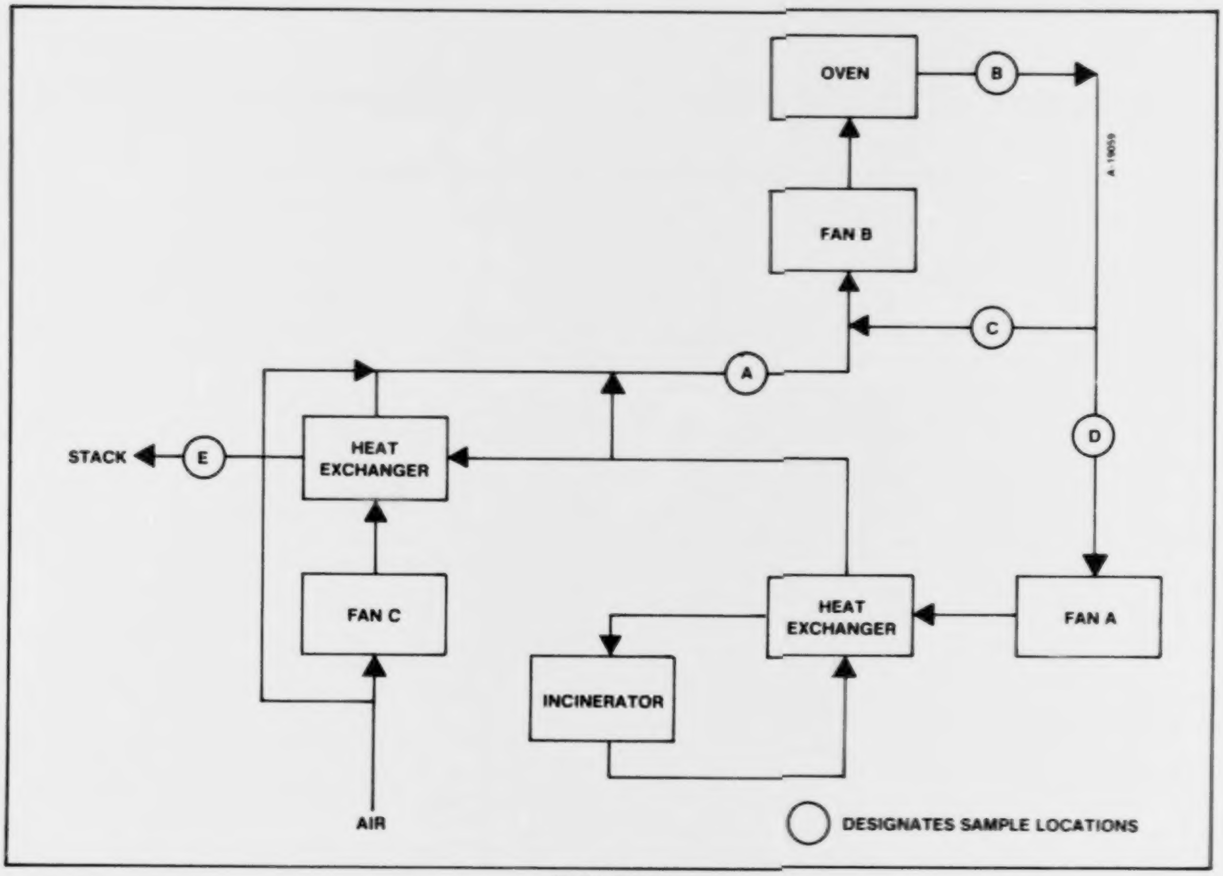

FIGURE 2

demonstrate a viable control concept that may reduce energy consumption of the manufacturing process and simultaneously destroy organic pollutants. Figure II describes this control design concept.

A third program involves the use of surfactant scrubbing technology. This concept has been undergoing laboratory research under EPA cosponsorship for approximately two years. We are now considering testing a pilot system in the field on a metal painting spray booth. If successful this technology may point the way to a low-cost efficient method of controlling extremely low concentration solvent-laden gas streams as may be found in paint spray operations.

Obviously, it is not possible to conduct research in all of the areas that may benefit from such programs. However, the aim of the present program is to attack the most urgent problem areas of the metal finishing industry. As new priorities are established and problem areas identified, IERL will continue to expand the scope of its efforts in air research and development for this industry.

Evaluation of Low Solvent Emission Degreasing Systems

Richard W. Gerstle, P. E., Vishnu S. Katari, P. E., & Robert L. Hearn*

INTRODUCTION

The term solvent degreasing refers to industrial cleaning processes in which nonaqueous solvents are used to remove soil from various metals, glass, plastic, and textile items. The major users of solvent degreasers are the automotive, electronics, and appliance industries, and others involved in metalworking. Solvent degreasing systems are also used in non-metalworking industries such as printing, chemicals, and plastics. In fact, most businesses use solvent metal cleaning processes at least occasionally, if not regularly. More than 1 million facilities routinely use solvent cleaning operations and large companies often have over 100 individual cleaning operations at one plant location.

In degreasing, a solvent in a liquid or vapor state is used to remove grease, oil, and dirt. There are two kinds of solvent degreasing: room temperature operations (cold cleaning) and vapor degreasing. Cold cleaning is the simplest and least expensive. The solvent is usually near room temperature; it may be heated if necessary, although the temperature must be held well below its boiling point. Then parts are cleaned by spraying, flushing, brushing, and immersion. Cold cleaning is a batch operation, but continuous operation is also practiced with conveyorized cold cleaning equipment. In vapor degreasing the solvent is heated to its boiling point, creating a zone of solvent vapor that displaces the air within the equipment to be cleaned. The parts are lowered into the vapor zone, where solvent vapors condense on them until the temperature of the parts approaches the boiling point of the pure solvent.

Vapor degreasing is performed by batch operation in open tank degreasers and by continuous operation in conveyorized degreasers. Of the estimated 30,000 vapor degreasers in use, 85 percent are open-top units, ranging in size from 1 by 2 feet up to 6 by 110 feet.

An open-top vapor degreaser emits 10 to 20 times as much solvent as would a typical cold cleaner, but less than half as much as a conveyorized degreaser.

Halogenated hydrocarbons are commonly used for vapor degreasing. Typical solvents are 1, 1, 1, trichloroethane, trichloroethylene, perchloroethelene, metheylene chloride, and fluorocarbons. All these solvents are toxic at sufficient levels. Recent studies conducted for the Environmental Protection Agency (EPA) show that reformulated petroleum solvents including perchloroethelene are photochemically reactive. Some of the halogenated degreasing solvents, such as 1, 1, 1 trichloroethane, are almost inert in the troposphere, but they may have an adverse environmental effect on the upper atmosphere.

During vapor degreasing, the solvent is emitted into the atmosphere as pure vapor. Because large numbers of degreasers are in operation nationwide, their solvent emissions contribute significantly to the total atmospheric loading of hydrocarbons. Solvent degreasing operations emit about 940,000 metric tons per year, a figure that represents about 4 percent of the annual total national volatile organic emissions from stationary sources. The proportion of solvent degreasing emissions is significantly higher in most urban areas because metalworking industries are concentrated in those areas.

Losses of solvent from the degreasing device and the consequent need to replace the solvent significantly affect the cost of degreaser operations. Control of emissions from solvent degreasers is sought, therefore, for both environmental and economic reasons.

Many open-top vapor degreasers, typically small or medium size batch-loaded degreasers, are operated in small manufacturing plants and job shops. Generally, degreasing is only an incidental step in the manufacturing operation. Such businesses cannot afford to apply expensive control systems to their degreasing operations. Nonetheless, minimizing solvent loss is a primary concern to these businesses because of the cost of replacing evaporated solvents. Since these same relatively small operations contribute significantly to the total of atmospheric emissions attributable to solvent degreasers, there is both public and private interest in developing emission reduction techniques that can be applied with minimal economic and environmental impacts.

Emissions from open-top vapor degreasers are due to diffusion, convection, carry out, leaks, and waste solvent disposal. Solvent vapors diffuse from the vapor zone at the air/vapor interface on the top of the vapor zone, and are carried into the atmosphere. Solvent vapors are lost through convection of warm solvent-laden air that passes upward and out of the degreaser. Solvent is lost through drag out of liquid and vaporous solvent when clean parts are extracted from the degreaser. Solvent emission will also result when waste solvent is disposed of in such a way that the solvent can evaporate into the atmosphere.

The evaporative solvent emissions can be reduced to a certain extent by any one of the following techniques:

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cleaning process changes, solvent degreasing equipment modifications, and solvent emissions control systems.

Good operating practices are the primary method of reducing carry out emissions. There are no general devices to minimize carry out from the open-top vapor degreasers.

Cleaning changes (such as water based alkaline washing metal cleaning method) or process changes such as liquid degreasing or conveyorized degreasing can be utilized, however, these methods will not substitute for vapor degreasing in all cases. Most of the items cleaned by vapor degreasing can not be cleaned by liquid degreasing. In some limited cases a conveyorized system can be substituted for two or more open-top degreasers. This can make the degreasing process less dependent on the operating personnel who may tend to overlook the requirements of minimizing pollution.

A typical degreaser includes a cover, a freeboard (minimum height is at least half the width of the degreaser), and a water condenser. But it has been a practice in the industry for the height of the freeboard to be three-quarters of the width of the degreaser when methelene chloride and trifluoroethelene are used. In most degreasers the bulk of the vapor is prevented from escaping the tank by condenser coils attached near the top of one or more of the walls of the tank. Open-tank degreasers of all sizes usually have water jackets with flowing water around the entire tank (above the coils) for further condensation action. The vapor loss is primarily dependent on the partial pressure at the condenser temperature. Even though tank covers are part of the original degreaser equipment, it is common for open-top systems not to be covered when idling or shut down. During this time, the amount of solvent vapor escaping to the atmosphere is related to its partial pressure. The convection losses are estimated to be anywhere from 0.05 to 0.1 lb/ft^2/hr for the open-top area. These losses are about 10 to 20 percent of solvent loss during both idling and operation of the degreaser. A significant portion of such emissions can be prevented by using covers. Previous EPA-sponsored tests that measured the effectiveness of covers on halogenated solvent consumption rates showed savings may range from 24 to 50 percent. All tests used the same equipment and solvent; the use of a cover was the only variable. On the basis of these limited test results, covers appear to be a wise investment even without considering air pollution control.

In the same test, increases of the freeboard ratio from 0.50 to 0.75 reduced solvent consumption by 27 percent. When slight drafts occurred, the comparative effectiveness of the larger freeboard increased in the same tests to 55 percent. These past tests tentatively indicate that significant increases in solvent efficiencies and significant reduction in pollution can be achieved by slight system modification. Increases in the size of degreaser freeboards can easily be accomplished by plant personnel or by degreaser equipment manufacturers. Equipment modifications such as increased freeboard height, refrigeration chillers and good maintenance and operating practice such as using covers during idling time and shutdown periods may achieve significant reduction of solvent emissions.

Further reduction in solvent loss from degreasers may also be achieved by refrigeration chillers. This is done by installing a second set of condensing coils in the degreaser. The refrigeration chiller which operates below or above 0° F temperature, creates a cold blanket above the vapor zone in the degreaser to prevent escape of the vapors. Vendor test data have been collected for refrigeration chillers operated at below freezing temperatures. The data show an emission reduction of an effective range of 16 to 60, with an average expectation of 40 percent. Installation and operation of a refrigeration chiller results in capital costs, and energy and utility costs. The operation of refrigeration chillers is either accompanied by a net profit or by a net additional cost, depending upon the size of the degreaser and its operation time. Tests showed that for a degreaser of 5 by 5 feet with a refrigeration chiller operating three shifts a day, the amount saved in solvent costs exceeded the additional operating costs of the refrigeration chiller. But for a comparatively smaller degreaser 2 by 6 feet operating only one shift per day, the amount saved in solvent costs was lower than the additional operating costs of the refrigeration chiller.

Equipment modifications or control devices may involve some additional investments for those who use degreasers; however, savings in solvent costs offset most of the annualized equipment cost and may even yield profit. In the past, a test program was conducted on the solvent emission reduction capabilities of different equipment modifications. But since this program was conducted under inconsistent test conditions, there was no method of correlating the data.

Following these earlier studies of controls for solvent degreasers, the EPA has undertaken a study to evaluate the pollution reduction capabilities of existing vapor degreasers and new developments in vapor degreasing systems and operations. EPA has contracted with PEDCo Environmental, Inc., to perform this study by testing selected degreaser systems with distinct features and thus generating data needed to evaluate the emission reduction capabilities of degreasers with various features and modifications. This program will generate data on atmospheric emission quantities for a variety of variables under carefully controlled operating conditions. The data will be reported in a form usable to federal, state and local air pollution agencies and industry. Evaluations will include economical and environmental impact studies.

The Project

The current study (conducted under EPA Contract No. 68-02-2535: Mr. Charles Darvin, Project Officer) will evaluate various degreasing systems in terms of their capabilities for reducing solvent emissions. A series of tests will be conducted under carefully controlled operating conditions to quantify atmospheric emissions. Degreasers for testing will include conventional devices with modifications as well as devices incorporating recent developments designed for reducing emissions. The data generated in the tests will be compiled and assessed in a report to EPA.

Project Approach

This project encompasses two principal tasks. The first is to prepare a detailed test plan describing the types of degreasers to be tested, the test site, test methods and variables, and the basis for technical and economic assessment of degreasers. Upon approval of this test plan by the EPA, PEDCo will perform the second task, which consists of conducting the tests in accordance with the plan and preparing a summary report.

Phase 1: Selection of Degreaser Units and Test Site

The total project will be performed in five phases. The first includes selection of the vapor degreasers for testing and selection of the test site. We will examine all vapor degreasers currently manufactured and observe their operation in order to select representative systems for testing. The selected systems will be altered in various ways to incorporate control features, which are basically the same for all vapor degreasers. These controls consist of a cover, a freeboard, and condenser coils, all of which are used to minimize solvent loss. A cover provides the easiest and most effective means of reducing the diffusion and convection of solvent vapors into the atmosphere. Most degreaser users, however, especially in small shops, do not use covers because it is inconvenient to do so, or because the degreaser is used frequently. A freeboard primarily serves to reduce drafts near the interface between air and the solvent vapor. The freeboard of a vapor degreaser is the distance from the top of the vapor zone to the top of the degreaser tank. OSHA established the required freeboard height. Condensor coils are positioned on the walls of the degreaser to condense the solvent vapors.

Recent developments in degreasing systems are believed to be capable of drastically reducing or eliminating solvent emissions. The effectiveness and the economic impacts of these developments have not yet been fully evaluated. Therefore, in selecting degreasers for testing, we will include one of conventional design, one modified by higher freeboard than is normally used and/or by lower condenser temperature, and one of new design for minimizing emissions. Several manufacturers have been contacted and have agreed to provide units for testing. When the size and specifications of the degreasers have been decided upon, manufacturers of the selected units will be contacted.

During the first phase, PEDCo will select a test site. The principal factor to be considered in site selection is the ability of the test team to accurately monitor solvent emissions and to control the test variables and operating conditions. Three test site options are available:

1) Equip a mobile testing facility for on-site testing of degreasers during operation,

2) Use equipment now set up for testing at various manufacturing facilities, or

3) Borrow degreasing equipment from manufacturers and ship it to the PEDCo test laboratory.

Logistics, quality control, and other considerations favor a single, centrally located test site. A mobile test facility would be expensive to operate and could not provide adequate control of ambient air unless the degreaser were installed in the vehicle. Although the use of a manufacturer's test facilities would provide accurate measuring devices and controlled surroundings, these test facilities vary considerably among manufacturers. Since the machines to be tested are of a size and type amenable to shipment at relatively low cost, testing of the several selected degreaser units at one well-equipped test facility seems most feasible.

Phase 2: Compilation of Process Variables

The second phase of the project involves compiling all of the process variables that may affect solvent emissions. Each of the variables must be distinguished from the process operating conditions that will be held constant. At the same time, various methods of measuring and analyzing hydrocarbon emissions, wastewater effluent, and sludge will be reviewed in order to ensure the use of the most accurate methods.

Many variables may affect emissions from vapor degreasers. Generally, these can be categorized as equipment related, operation related, and ambient related. Equipment-related variables are the most effective controls for open-top vapor degreasers. As discussed earlier, the major controls consist of covers, freeboards, and condensers, all of which can be modified in various ways. The other equipment-related variables to be considered are geometry of parts to be cleaned (specific surface area and length/diameter ratio, for example). Operation-related variables that may affect solvent emissions include type of solvent, solvent temperature, operating cycle, load, heat balance, and air crosscurrents. Finally, ambient conditions in the degreasing area may also contribute to the escape of solvent vapors, e.g., air movement, ventilation, and humidity.

Because it would be impossible to test and determine the effects of all variables on solvent emissions, these variables will be classified and statistically analyzed to determine the most appropriate means of quantifying their cumulative impacts upon emissions. Factors that have the most significant effects on emissions will be given priority. The number of variables to be tested will, however, be limited because of time constraints. Factors with only slight effects on emissions will be held constant to provide standard operating conditions and a consistent basis for comparing test results. To ensure that all relevant design factors and variables are included in the test plan, PEDCo will review all pertinent reports and documents and will consult with knowledgeable persons and organizations.

Phase 3, 4 and 5

The third phase of the project is preparation of a report summarizing the test plan, including full analysis of the overall test design. This information will be condensed into an EPA Capsule Report for industry-wide distribution. Phase 4 will be the testing of selected vapor degreasing systems in accordance with the approved test plan. Concurrently, we will perform Phase 5, which involves reduction and analysis of the data. Emission data will be related to the operating parameters of the degreaser systems so that the need for additional data can be recognized and accommodated while the units are still undergoing tests. On the basis of test data, the economic and environmental impacts of each degreaser system will be evaluated to determine their capabilities for low-solvent emissions under comparable conditions. A summary report presenting test conditions, procedures, results, and conclusions will conclude the project.

Summary

The principal purpose of this study is to evaluate the capabilities of existing solvent degreaser systems for reducing solvent emissions and to determine the environmental and economic impacts of various control measures.

From an environmental standpoint, an investigation of this kind will assist both manufacturers and users of degreaser systems in identifying and minimizing solvent losses, which constitute a major source of hydrocarbon emissions. Very little quantitative data are available with which to evaluate the emission reduction capabilities of existing degreaser systems. Although vendors of new solvent degreasing control systems on the market claim that these systems are highly efficient, little information is available to support these claims. Where emission data are available, they are difficult to evaluate because tests are often based upon different operating conditions, assumptions, and test procedures.

From an economic standpoint, this study should aid the users of solvent degreasers in identifying what is required of them to achieve adequate emission controls. In particular, this study should define for the small manufacturer and job shop operator the measures that are most effective in reducing solvent losses and therefore reducing operating costs.

REFERENCES

1. Emission Standards and Engineering Division, Chemical and Petroleum Branch, U. S. EPA. Control of volatile organic emissions from organic solvent metal cleaning operations (draft document). Research Triangle Park, North Carolina, April 1977.
2. The Dow Chemical Company. Study to Support New Source Performance Standards for Solvent Metal Cleaning Operations. EPA Contract No. 68-02-1329. U. S. Environmental Protection Agency, April 30, 1976.
3. JACA Corporation. Air Pollution Control of Hydrocarbon Emissions - Solvent Metal Cleaning Operations. U. S. Environmental Protection Agency.

Minimizing Energy Use in Solvent Incineration

Thomas C. Ponder, Jr.*

INTRODUCTION

The metal finishing industry uses organic coatings to protect or decorate bare metal. The coating processes release volatile organic compounds (VOC) to the atmosphere in the form of aerosols, or gases. Although there are several methods of reducing these emissions, this presentation will deal only with thermal incineration equipment, which converts the organics (mostly hydrocarbons) to water vapor and carbon dioxide by combustion. The devices used are commonly called "afterburners."

Although afterburners provide one of the most effective methods of controlling hydrocarbons, they can consume substantial amounts of fuel, mainly distillate oils or natural gas (electric heat has also been used). Since the oil embargo of 1973, the Federal Government has urged conservation of these resources, placing industry in a dilemma between protecting the environment and conserving energy. This has caused increasing interest in heat recovery from afterburners.

Heat recovery can be applied to almost every afterburner. Heat recovery is not 100-percent efficient but in some cases energy contained in the waste stream (from solvents) is so high, the afteburner with heat recovery can actually use less fuel than would be required if no afterburner were used.

In this paper, I will describe the types of heat recovery systems offered, and name the major manufacturers. The efficiency of each type of system will be discussed, together with the relative cost. Limitations and advantages of each system will also be covered.

Process Description

The use of an afterburner involves two unit operations, combustion and heat transfer. Combustion is rapid oxidation; it requires a combination of an oxidizable material, an oxidant, and sufficient heat to start and maintain burning. In this case the oxidizable material is the VOC, and oxygen (from the air) acts as the oxidant. Operators are compelled by National Fire Protection Association (NFPA) codes to dilute VOC to 25 percent of the lower explosive limit for the exhaust stream, so heat must be supplied to effect combustion of these compounds. (Higher concentrations are possible if proper fail safe methods are used.)

Afterburners commonly employ one of two types of combustion processes, thermal or catalytic. The thermal process usually requires temperatures in excess of 1200° F for retention times of 0.5 second. Time and temperature, however, are dependent on the concentration of the organic compound. Catalytic processes, on the other hand, generally require temperatures of 900° F or less, since the catalyst effects combustion at lower temperatures.

Products resulting from incomplete combustion are detectable in the flue gas as: 1) carbon monoxide (instead of carbon dioxide, which is the fully oxidized form); 2) VOC; and 3) organic particulate matter.

Heat recovery efficiency of an afterburner cannot be 100 percent. The main energy loss is from the fact that combustion products leave the system at much higher than process inlet temperatures, even after heat recovery. Other energy losses from an afterburner result from incomplete combustion and heat losses through the combustion chamber walls. These losses seldom exceed 1.5 percent of the input heat to the afterburner.

Heat Transfer and Recovery

Heat recovery for afterburners is the transfer heat energy by a device from the higher-temperature exhaust stream to the lower-temperature inlet stream. The minimum exhaust temperature is kept above the dew point of the exhaust gases to avoid condensation of corrosive products. The dew point of natural gas-fired exhaust is about 90° F and that of distillate fuel oil-fired exhaust is about 160° F to prevent the condensation of corrosive sulfuric acid. In practice, it is not economical to achieve such temperatures so dew point is rarely a problem.

HEAT RECOVERY SYSTEMS

Heat recovery devices are classified by their mode of heat transfer, i.e., direct or indirect. The mixing chamber is an example of a direct device, in which mixture of high and low temperature streams produces 100-percent heat recovery. This system is shown in Figure 1.

Indirect heat recovery systems, classified as either "recuperative" or "regenerative", do not mix the streams. Tubular air heaters, economizers, and heat recovery boilers are all examples of recuperative heat recovery. Heat recovery in these devices is limited by the thermal conductivity of the barrier and the heat transfer fluid. Air-to-air heat exchangers are the most frequently used type of heat recovery device, primarily because they are simple and have no moving parts.

Figures 2 and 3 illustrate single-pass recuperative heat recovery in the cocurrent and countercurrent gas flow

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PEDCo Environmental, Inc.

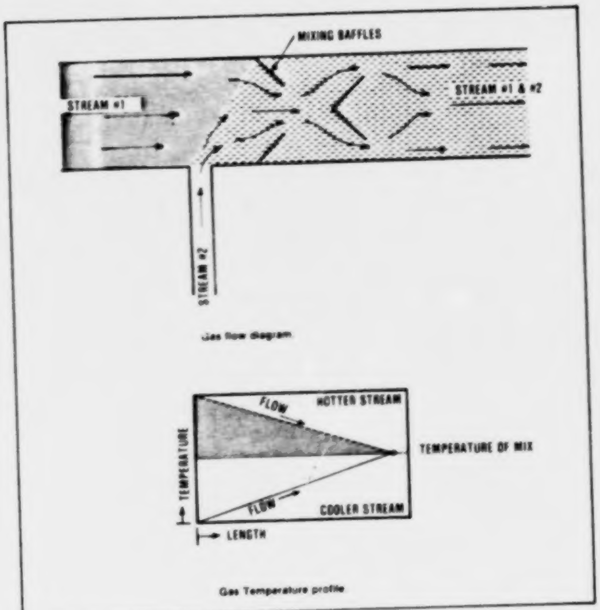

MIXING BAFFLES
STREAM #1
STREAM #1 & #2
STREAM #2
Gas flow diagram
FLOW
HOTTER STREAM
TEMPERATURE OF MIX
TEMPERATURE
FLOW
COOLER STREAM
LENGTH
Gas Temperature profile

Fig. 1—Heat recovery with a mixer.

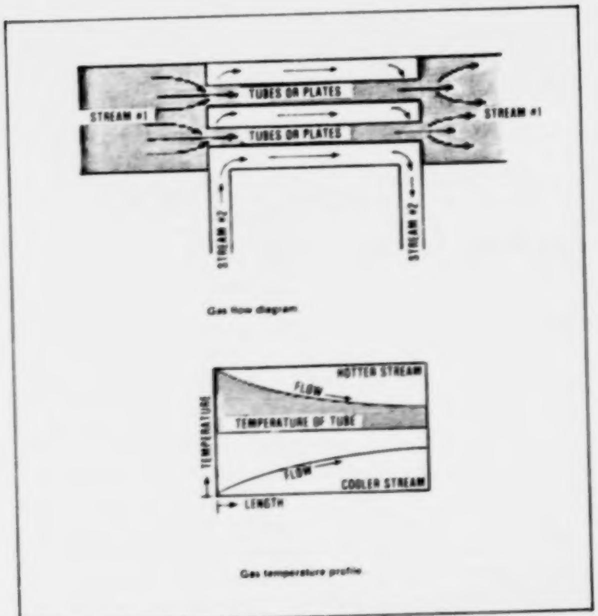

TUBES OR PLATES
TUBES OR PLATES
STREAM #1
STREAM #1
STREAM #2
STREAM #2
Gas flow diagram
HOTTER STREAM
FLOW
TEMPERATURE OF TUBE
TEMPERATURE
FLOW
COOLER STREAM
LENGTH
Gas temperature profile

Fig. 2—Heat recovery with cocurrent flow recuperator.

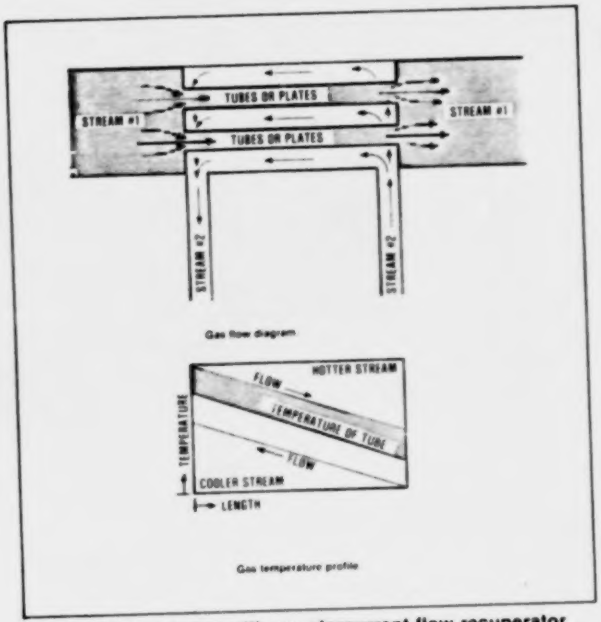

TUBES OR PLATES
TUBES OR PLATES
STREAM #1
STREAM #1
STREAM #2
STREAM #2
Gas flow diagram
HOTTER STREAM
FLOW
TEMPERATURE OF TUBE
TEMPERATURE
FLOW
COOLER STREAM
LENGTH
Gas temperature profile

Fig. 3—Heat recovery with countercurrent flow recuperator.

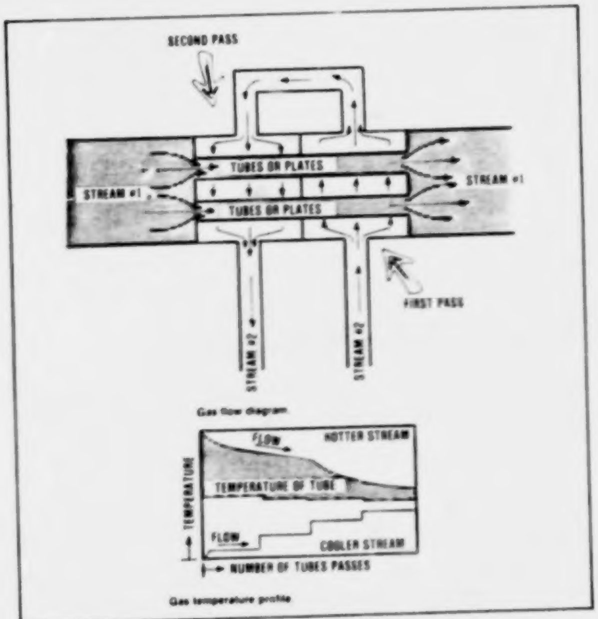
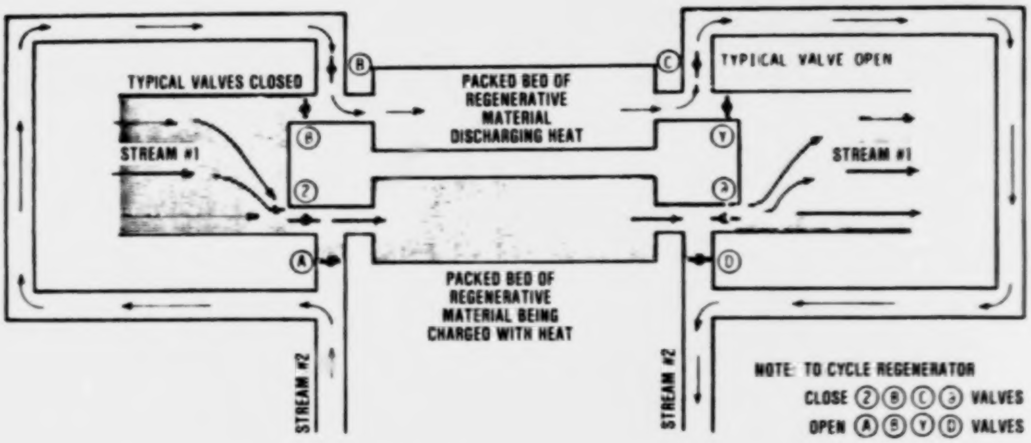

SECOND PASS
TUBES OR PLATES
TUBES OR PLATES
STREAM #1
STREAM #1
FIRST PASS
STREAM #2
STREAM #2
Gas flow diagram
FLOW
HOTTER STREAM
TEMPERATURE OF TUBE
TEMPERATURE
FLOW
COOLER STREAM
NUMBER OF TUBES PASSES
Gas temperature profile

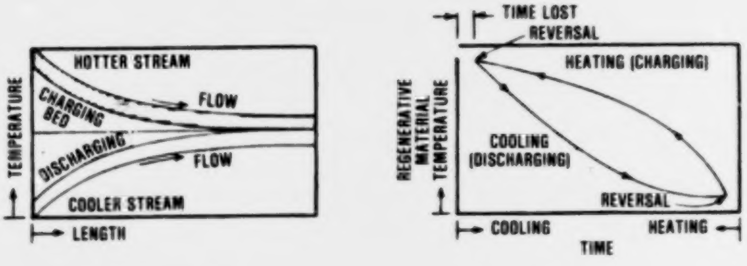
Fig. 4—Heat recovery with cross flow recuperator

mode. Maximum theoretical heat recovery for cocurrent is 50 percent where the flows and fluids are identical. Maximum theoretical heat recovery for countercurrent is 100 percent. Maximum heat recovery for countercurrent depends on many factors but the economic optimum is usually 50 percent. Cross-flow is between the two. Figure 4 illustrates a two-pass recuperative system in which economical heat recovery is usually about 70 percent.

Regenerative devices generally achieve greater heat recovery than recuperative exchangers. They do this at non-uniform rates through the use of a heat-absorbing material that stores the heat for reuse. This material is thermally recycled, i.e., charged with heat and then discharged. Two or more devices may be combined to provide a more uniform recovery temperature. The regenerative material may be either stationary, with the


TYPICAL VALVES CLOSED
B
PACKED BED OF REGENERATIVE MATERIAL DISCHARGING HEAT
C
TYPICAL VALVE OPEN
β
γ
STREAM #1
STREAM #1
2
3
A
D
PACKED BED OF REGENERATIVE MATERIAL BEING CHARGED WITH HEAT
STREAM #2
STREAM #2
NOTE: TO CYCLE REGENERATOR
CLOSE ② Ⓑ Ⓒ ③ VALVES
OPEN Ⓐ β γ Ⓓ VALVES

Gas flow diagram.



With generator length

With time

Gas temperature profiles.

Fig. 5—Heat recovery with cyclic regenerator.

hot and cold gas streams alternated between multiple chambers packed with the material; or the regenerative material may rotate, e.g., as a metal or ceramic wheel between hot and cold streams (Figure 5 and 6). Table 1 is a list of the systems offered, their stages of recovery, use of heat recovery, and the number of vendors offering each system.

Appendix A lists the major manufacturers of heat recovery systems and the types of system each offers.

Advantages and Disadvantages

Heat recovery from afterburners has advantages and disadvantages. In general, they are as follows:

Advantages

1. Reduced energy consumption
2. Reduced overall costs

Disadvantages

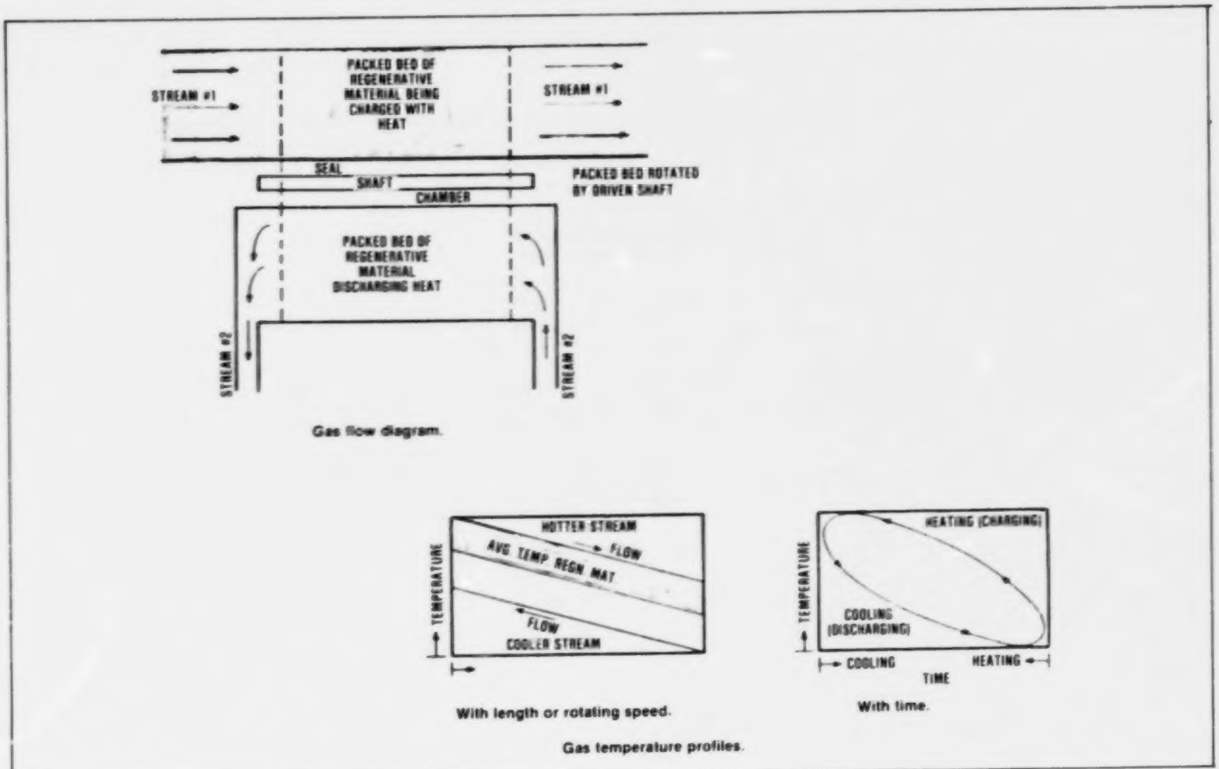
1. Clean waste streams required
2. Increased capital costs
3. Control is complicated
4. Space requirements

Although afterburners reduce energy consumption and costs, relatively clean exhaust streams are needed to prevent plugging. Highly pigmented paints, for example, can foul even the simplest recuperative heat exchanger. Capital costs rise with the addition of heat recovery equipment. In addition, control of an afterburner equipped for heat recovery can be more difficult than a simple afterburner. In many cases, too, the plant has insufficient space to install the heat recovery equipment.

Table 2 describes the advantages and disadvantages of various heat recovery methods: gas mixing (recycle), recuperative, (waste heat boiler), recuperative (air to air), regenerative (rotary), and regenerative (fixed bed). The sections that follow discuss the pros and cons of each heat recovery method.

Gas Mixing (Recycle)

Gas mixing is commonly used in recycling combustion gases to curing ovens. This process has the highest efficiency if 100 percent recycle were possible since this


STREAM #1
PACKED BED OF REGENERATIVE MATERIAL BEING CHARGED WITH HEAT
STREAM #1
SEAL
SHAFT
CHAMBER
PACKED BED ROTATED BY DRIVEN SHAFT
PACKED BED OF REGENERATIVE MATERIAL DISCHARGING HEAT
STREAM #2
STREAM #2
HOTTER STREAM
FLOW
AVG TEMP REGN MAT
FLOW
COOLER STREAM
TEMPERATURE
HEATING (CHARGING)
COOLING (DISCHARGING)
TEMPERATURE
COOLING
HEATING
TIME

Gas flow diagram.

With length or rotating speed.

With time.

Gas temperature profiles.

Fig. 6—Heat recovery with heat wheel regenerator.

TABLE 1
TYPES OF HEAT RECOVERY SYSTEMS

Type of recovery system	*Heat recovery component*	*Typical use for recovered heat*
Gas mixing	Recycle of portion of combustion exhaust gases	Drying oven
Recuperative	Gas to gas heat exchanger	Preheat combustion feed gas Provide heat for building, dry-off oven or other use
Recuperative	Waste heat boiler or economizer	Generate steam and or superheated steam Provide hot water Recirculate heated thermal fluid to various heat users
Regenerative	Metal rotary exchanger Ceramic rotary exchanger Packed bed	Preheat combustion feed gas

would require no heat exchange surface. This is not possible, however, due to condensation, sulfur in the fuel, particulate, and reduced oxygen levels.

Recuperative (Tubular)

The primary advantage of the tubular recuperative heat exchanger is its low capital cost and simplicity. This system has several disadvantages, including low efficiency, leakage from differential thermal expansion, and bulk and weight. The metal surfaces are easily fouled by hydrocarbons and require maintenance and frequent cleaning. The hot tubular surface can polymerize resins, causing reduced heat transfer and possible combustion on the heat exchanger surfaces. Condensation corrosion is also a problem, since the heat exchangers are normally made of carbon steel.

Recuperative (Waste Heat Boilers)

The primary advantage of waste heat boilers is their transfer of heat energy into a more easily transported medium. Their efficiency is usually higher than that of simple tubular exchangers. Waste heat recovery as steam requires the VOC producing process and steam using equipment to operate in synchrony unless provisions are made for steam production while the VOC producing process is down. Finally, condensation corrosion is a problem in waste heat boilers.

TABLE 2. TYPES OF HEAT RECOVERY

Type	Efficiency percent	Additional auxiliary equipment	Limitations, problems	Commonly used for	Commonly not used for
Tubular exchanger Gas/gas Cross-flow	1 stage-50% max 2 stage-62% max		1) May be easily fouled; frequent cleaning and maintenance. 2) Failures, differential thermal expansion. 3) Bulky, heavy, added roof load and/or floor space. 5) Corrosion if cools below dew point of flue gas.	Resin curing ovens Paint drying ovens Chemical plants	Rendering plants*
Regenerative (rotary) exchanger	Up to 85%		1) Easily fouled. Use only on relatively clean streams. 2) Burnout if failure on rotary drive motor. 3) Requires attention to pressure balance to control leakage at seals. 4) Avoid cooling flue gas to dew point, but otherwise is relatively insensitive to corrosion.	Odor control, water treatment units Power plants	Any fumes containing oils, dusts, resins
Flue gas recycle to oven	30%	Safety controls	1) Process must be compatible with flue gas (condensation? Sulfur in fuel? CO or CO_2? Reduced oxygen? Unburned fuel?) 2) Usefulness depends on temperature and heat requirements of fume generating process.	Resin, lacquer curing ovens, (if low solvent release) Litho ovens	Varnish cookers (combustibles hazard) ovens requiring human access. Smoke ovens (low temperature)
Steam generators, boilers, water heaters	to 75%	Extra burners and controls; safety controls Extra ducting, blowers, controls	1) May tie steam generation to fume process and vice versa. 2) Match steam heating load to afterburning heat release. 3) Condensation on cold-water coils.	Plant steam supply CO burner and boiler (fluid bed catalytic cracking unit in oil refinery. Uses supplementary fuel firing) Plant heating and air conditioning units	
Process heat-via circulating heat transfer salt (Hytec), oil, air	to 75%	Exchangers, piping, reservoir, pump, controls	1) Ties fume generation to process. 2) Matches process heat load to afterburner heat release (but can use supplementary firing for added process heat).	Asphalt blowing, preheating	

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* One manufacturer claims to have used heat exchangers successfully for rendering plants.

Regenerative (Rotary)

The primary advantage of the regenerative exchanger is its potential for high efficiency. Shortcomings include easy fouling, high maintenance necessary to prevent shortcircuiting across heat exchanger seals and burnout if the rotating motor fails.

Regenerative (Fixed Bed)

The advantages of this system are high efficiency and insensitivity to precombustion in regenerative packing. Disadvantages include large space requirements, and a complicated valving system requiring much maintenance.

HEAT RECOVERY COSTS

This section contains the costs of several actual heat recovery systems. These examples are not aimed at showing which systems are always the most economic. In actual practice, each type of heat recovery should be evaluated for the actual conditions of the source being controlled. For economic comparison, the process stream will be shown with a simple afterburner, and with an afterburner with heat recovery.

Recuperative (Indirect Recycle) Recovery System

This system contains a two-pass recuperative heat exchanger to preheat the exhaust stream from an aluminum coil coating operation. The system also includes a fourpass recuperative exchanger to provide makeup air for the coil coating operation. It has an overall heat recovery from the afterburner of 85.8 percent, with a reduction in fuel requirements of 75 percent. As shown in Table 3, the capital cost of the system is $426,000 in January 1977 dollars and the annual operating cost is $127,000, which represents a savings of only $10,000, i.e. a return on incremental cost of only 3.7 percent when compared with the costs of a simple afterburner system. Thus, this heat recovery system is probably not economically justified.

TABLE 3
RECUPERATIVE HEAT RECOVERY SYSTEM

	Capital cost	*Annual cost*
Heat recovery system with afterburner	$426,000	$127,000
Simple afterburner without heat recovery	$155,800	$137,000
Savings		$ 10,000
Return on incremental investment, percent		3.7
Capital cost/acfm		$36.50
System size, acfm		11,670

TABLE 4
REGENERATIVE (FIXED BED) RECOVERY SYSTEM WITH RECYCLED HEAT

	Capital cost	*Annual cost*
Heat recovery system with afterburner	$435,000	$104,000
Simple afterburner without heat recovery	$154,000	$183,000
Savings		$ 79,000
Return on incremental investment, percent		28.18
Capital cost/acfm		$ 21.75
System size, acfm		20,000

Regenerative (Fixed Bed) Recovery System with Recycle

This system contains a three bed regenerative heat exchanger to preheat the exhaust stream from a steel coil coating operation. Part of the exhaust gases are recycled to the oven. This system has an overall heat recovery from the afterburner of 96.2 percent, with a reduction in fuel requirements of 97.2 percent. As shown in Table 4, the capital cost of the system is $435,000 in January 1977 dollars, and the annual operating cost is $104,000. When compared with a simple afterburner system, the savings is $79,000, or a return on incremental cost of 28.18 percent. This heat recovery system, therefore, can be economically justified.

Regenerative (Rotary) Recovery System With Waste Heat Boiler

This system contains two rotary regenerative heat exchangers, which use high temperature exhaust from the afterburner to heat makeup air to a metal coating operation. The system also uses some of the high-temperature exhaust as partial input into a boiler. This system has an overall heat recovery from the afterburner of 98.5 percent. Since there is more heat from the afterburner than the coating system can use, afterburner heat supplants part of the plant boiler's fuel requirement. As shown in Table 5, the capital cost of the system is $949,000 in January 1977 dollars; the annual operating cost is $640,000. Because of the complex nature of this system, data were insufficient to calculate the savings obtained in comparison with the cost of a simple afterburner.

Recuperative (Direct Recycle) Recovery System

This system contains a single-pass recuperative heat exchanger to preheat the exhaust stream from a metal litho operation. This system also includes partial recycle of the exhaust stream to preheat the curing oven. It has an overall heat recovery from the afterburner of 89.7 percent, with a reduction in fuel requirements of 77.3 per

TABLE 5
REGENERATIVE (ROTARY) RECOVERY SYSTEM WITH WASTE HEAT BOILER

	Capital cost	*Annual cost*
Heat recovery system with afterburner	$949,000	$640,000
Simple afterburner without heat recovery	$172,000	$168,000
Savings		None
Return on incremental investment, percent		None
Capital cost acfm		$ 31.63
System size, acfm		30,000

TABLE 6
RECUPERATIVE (DIRECT RECYCLE) HEAT RECOVERY SYSTEM

	Capital cost	*Annual cost*
Heat recovery system with afterburner	$233,000	$ 64,500
Simple afterburner without heat recovery	$ 91,200	$ 59,000
Savings		None
Return on incremental investment, percent		None
Capital cost acfm		$ 38.83
System size, acfm		6,000

TABLE 7
RECUPERATIVE (WASTE HEAT BOILER) HEAT RECOVERY SYSTEM

	Capital cost	*Annual cost*
Heat recovery system with afterburner	$567,500	$214,500
Simple afterburner without heat recovery	$127,000	$115,000
Savings		None
Return on incremental investment, percent		None
Capital cost acfm		$ 54.00
System size, acfm		10,500

cent. The capital cost of the system is $233,000 in January 1977 and the annual operating cost is $64,500 (Table 6). The system would not show a savings when compared with the costs of a simple afterburner.

Recuperative (Waste Heat Boiler) Heat Recovery System

This system contains a single-pass recuperative heat exchanger to preheat the exhaust stream from an aluminum can production line. It also includes a waste heat boiler to preheat water for can washing. The system has an overall heat recovery from the afterburner of 68.0 percent, with a reduction in fuel requirements of 52.0 percent (Table 7). The capital cost of the system is $567,500 in January 1977 dollars, and the annual operating cost is $127,000. It has no cost advantage over a simple afterburner.

APPENDIX A
List of Companies and Industry Contacts for Available Heat Recovery Systems or Components

Company and Contact	*Type Systems and Components*
Surface Combustion Division Midland-Ross Corporation 2375 Dorr Street Toledo, Ohio 43691 Phone Number: (419) 536-4611 TWX 810-442-1651 T. V. Bettinger, Sales Manager Thermal Process Systems Tom Schultz Dean Schmidt	Recuperative, recycle
C. E. Air Preheater Combustion Engineering, Inc. Post Office Box 372 Wellsville, New York 14895 Phone Number: (716) 593-2700 C. E. Pauletta, Manager Special Applications	Regenerative, recycle, recuperative
Oxy Catalyst, Inc. Research-Cottrell, Inc. East Biddle Street West Chester, PA 19380 Phone Number (215) 692-3500 K. Allen Napier, Sales Engineer	Recuperative, recycle
Air Correction U. O. P. Darien, Connecticut 06820 Phone Number: (203) 655-8711 G. L. Brewer, Product Sales Manager Steve Olson, Sales Engineer	Recuperative, recycle, Heat recovery boilers
Engelhard Industries Systems Department 2655 U. S. Route 22 Union, New Jersey 07083 Phone Number: (201) 589-5000 Martin F. Collins, Manager Air and Gas Systems	Recuperative, recycle

(Continued on next page)

APPENDIX A
List of Companies and Industry Contacts for Available Heat Recovery Systems or Components

Company and Contact	*Type Systems and Components*
Matthey-Bishop, Inc. Malin Road Malvern, PA 19380 Phone Number (215) 644-3100 J. H. Povey, Marketing Manager Thomas H. Snape, Product Specialist	Recuperative, recycle
Granco Equipment 1958 Burlingame, S. W. P. O. Box 1767 Grand Rapids, Michigan 49501 Phone Number: (616) 241-5603 Charles B. Gentry, President	Regenerative, recycle
REECO Regenerative Environmental Equipmnt Co., Inc. P. O. Box 600 520 Speedwell Avenue Morris Plains, NJ 07950 Phone Number: (201) 538-8585 J. Mueller, President	Regenerative
Allied Air Products Co., Inc. 315 E. Franklin Newberg, Oregon 97132 Phone Number: (503) 538-8341 TELEX 360 423 William F. Zunker, Vice President Sales & Marketing	Recuperative
Trane Thermal Company Brook Road Conshohocken, PA 19428 Phone Number: (215) 828-5400 John J. Sudnick, Sales Engineer Process Systems	Incineration with recuperative heat recovery
KENTUBE 4150 South Elwood Tulsa, Oklahoma 74107 Phone Number: (918) 446-4661 TELEX 4-2353 Jerry Herrington, Administrative Sales Engineer	Recuperative

APPENDIX A
List of Companies and Industry Contacts for Available Heat Recovery Systems or Components

Company and Contact	*Type Systems and Components*
Eclipse Lookout Company A Division of Eclipse, Inc. P. O. Box 4756 Chattanooga, TN 37405 Phone Number: (615) 265-3441 TELEX 558-427 Don Fillers, Heat Recovery Sales Manager	Incineration with recuperative heat recovery, boilers
Heat Recovery Corporation 590 Belleville Turnpike Kearney, NJ 07032	Recuperative
Q-Dot Corporation 151 Regal Row Suite 220 Dallas, TX 75247 Phone Number: (215) 630-1224 TELEX 730365	Regenerative for use in HVAC systems
Voss Finned Tube Products, Inc. 4832 Ridge Road Cleveland, OH 44144 Phone Number: (216) 398-8100 TELEX 810-412-8223	Recuperative
Deltak Corporation 13330 - 12th Ave., North Xenium at 12th Avenue Minneapolis, Minnesota 55440 (Mailing Address) P. O. Box 9496 Minneapolis, Minnesota 55440 Phone Number: (612) 544-3371 TELEX 29-0812 Gary G. Steele, Sales Engineer	Recuperative heat recovery boilers
Smith Environmental Corp. 1903 Doreen Avenue P. O. Box 3696 South El Monte, CA 91733 Phone Number: (213) 686-2155 (213) 443-0214 (213) 443-0214 J. M. Archibald, Vice-Pres.	Incineration with recuperative exchangers

An Overview of the EPA R&D Program For Water Pollution Control In the Metal Finishing Industry

Mary K. Stinson*

The net effect of many different Federal and local laws and regulations in force or to take effect in the future is to place increasingly strict limits on the levels of various substances that can be discharged into wastewaters. Other Federal and local laws and regulations place increasingly strict limits on the way in which such products as sludges from wastewater treatment can be disposed of. The direction in which these Federal and local laws and regulations are guiding the metal finishers is toward a system of materials recovery — the only route left open.

This paper discusses how EPA water recycling and research projects are accompanying the metal finishing industry toward that system of materials recovery. Another point that I would like to make is the importance to conserve our natural resources.

As an example of laws that have begun to move the industry in this direction, the Federal Water Pollution Control Act (Public Law 92-500) does or will require that the metal finishing industry like all other industries remove certain levels of certain pollutants from its wastewaters before they are discharged either to a municipal system or a receiving water. Some guidelines for this industry have been established already. Other guidelines for direct discharge as well as pretreatment are still being considered.

The EPA is well aware of the complexity and diversity of this industry and of the technical and economic problems inherent in applying pollution abatement technology to its processes.

It has been estimated[1] that there are at least 70,000 facilities in the U. S. which are involved either in simple or complex metal finishing operations. These facilities employ a total of 600 different processes. The list of pollutants regulated to date is not very long. As a matter of fact, due to the complexity of the industry and the variety of metals and reagents used, all pollutants may never be regulated. However, it is anticipated that some additions of other pollutants to this list will be made in the future as new and different environmental regulations are enforced.

EPA's R&D Office carries out developmental and/or demonstration programs which attempt to demonstrate methods to reduce some of the major problems of this industry. Our overall goal has always been to assist the industry in meeting its current as well as future regulations. Also, we encourage the development and demonstration of technology that shows promise of a long-term solution to the problem, provides economic incentive to the user, conserves our national resources, and does not cause other environmental problems.

Selection of the individual projects, or technologies for development is done by EPA's staff familiar with the industry and very often with assistance of the members of the industry themselves or represented by AES or MFF. The intent is to foster accelerated development of sound ideas, to assume some of the risk inherent in any new system, and to expose the technical community to the subject technology. In practice, grants and contracts can be awarded to universities, research firms, or in the case of demonstration projects, the actual user of the new technology. The product is a report fully documenting the results. Successful full-scale demonstrations are most rewarding in that the technology is often employed as a part of wastewater and/or recovery treatment at the given facility even after the project is completed. Examples are some completed projects.

As far as technology is concerned, EPA's R&D co-sponsors projects ranging from chemical destruction to physical-chemical concentration and recovery. The most

SLIDE 1
U. S. METAL FINISHING INDUSTRY

70,000 facilities
600 processes
High water use

Chemicals and large fraction of metals are discharged to the environment.

Major wastestreams:

1. accidental spills
2. spent processing solutions
3. rinsewaters

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extensive list of EPA projects for treatment of metal finishing wastewaters and their brief review is given in Dr. Skovronek's and my paper[2] published in October's and November's issues of Plating as Part I and II. These projects include state of the art surveys, laboratory investigations, pilot plant testing, and full-scale demonstration on an operating line.

Questions now arise as to what is the actual impact of all these technologies, how can they really help the industry as a whole, and where do we go from here with our research program? Research completed to date as well as preliminary results from ongoing projects have already begun to form a picture of the impact these technologies will have on industry. This work also throws a little light down the road we all will be traveling in the future.

To date, most of the industry has used what can be called conventional technology to meet the current requirements. It is these conventional technologies, largely precipitation, which have led to the current and future problems with sludges. It is generally believed that conventional treatment is adequate and often the most cost-effective. Yet it is a temporary measure in many instances and it is a straight forward cost, offering no economic benefit or incentive.

As for the adequacy of conventional treatment there are many instances where this treatment is not reliable. The systems are labor intensive and subject to employee error. In the case of heavy metal removal by precipitation, careful pH control and other process controls are needed to avoid solubilization of residuals by ammonia and chelating agents which would interfere with the precipitation reaction. These ideal conditions are not easily maintained and not all interferences are easily established. Both AES and MFF recognize the need for studies that would identify and remove interferences that cause sudden excursions of metals in the treated effluent. Meanwhile our program has an ongoing study that will result in a manual presenting all aspects of the techniques of conducting precipitation of metals from wastewaters most effectively.

SLIDE 2
DEMONSTRATED TECHNOLOGIES IN OPERATION

Facility	*Technology*	*Comment*
Beaton & Corbin	Integrated Treatment	
Anaconda	Cementation	Recovery of copper and reduction of hexavalent chromium
New England Plating	Electrolytic	Oxidation of cyanide and reduction of chromium
Sealectro Corp.	Ozone	Oxidation of cyanide
Advance Plating	Evaporation	Recovery of chromic acid

Some local environmental regulations may be stricter than the Federal ones and the conventional treatment may not be adequate there. Some sewer ordinances are very strict. An example is a sewer ordinance of the City of Taunton, Massachusetts which sets very low levels for heavy metals and cyanide.[3]

Municipal sewer ordinances may also prohibit acceptance of cadmium-bearing wastewaters unless high removals are achieved at the source. Conventional treatment generated sludges containing the very heavy metals we wish to remove from environment such as Cu, Zn, Ni, Cd, Cr, etc. Cadmium is a particularly undesirable component of the municipal sludge and may be a limiting factor in the agricultural disposal of this sludge. The sludge generation and disposal problem cannot be discounted or ignored. If dewatering of sludges is required, the cost of treatment increases. Also, in some states there may be no nearby landfill area that would accept this sludge. In the Commonwealth of Massachusetts, metal finishing sludge cannot be landfilled at all. Recovery of metals, particularly from mixed metal sludge, is not economically feasible at this time.

Resource conservation is another aspect that should concern us all. The metal finishing industry consumes almost all commercially important metals, but due to the inefficiency of the processes employed and other reasons such as changes in the spent processing solutions, large fractions of the metals end up in wastewaters. According to a recent article[4] in Metal Progress, the U. S. must import a large number of commercially important metals and ores. More than 90% of palladium and chromium, and more than 50% of tin, nickel, zinc, antimony, and tungsten must be met by imports. Recovery of noble

SLIDE 3
EXCERPT FROM A SEWER ORDINANCE OF THE CITY OF TAUNTON, MA

Substance	*Maximum Concentration Allowable in Milligrams per Liter*
Arsenic	0.1
Cadmium	0.2
Chromium (Total)	1.0
Copper	2.0
Cyanides	1.0
Lead	1.0
Mercury	0.01
Nickel	1.0
Silver	1.0
Zinc	3.0

metals and of several other high-priced metals already has been practiced by the industry. Savings are not only in the recovered metals alone but also in the avoidance of sludge generation, ease in meeting discharge or pretreatment regulations and in reduction of the Country's dependence on imports. Recovery of metals from wastes also is often less energy intensive than production of primary metals from ores. Recovery of cadmium, for example, from wastewaters may present additional benefit of complying with regulations for toxic substances.

It is in techniques where both water and reagent conservation and recovery can be practiced that one can begin to see a long-term solution and even a payout. We all know that except for recovery of noble metals such as gold, any recovery technique is more expensive than no treatment at all. However the reality of the present is that "no treatment" is no longer a viable alternative.

Let's now have a look at some of our programs. In general the majority of our projects have been concerned with recovery of either a metal or another reagent of importance and water.

Our involvement in reverse osmosis (R. O.) spans seven years, and we have participated in nine projects. Two are surveys, two laboratory investigations, three field tests, and finally the most recent one is a design, construction and field testing of a full scale mobile unit. We can now say that early EPA-AES participation in the reverse osmosis development program speeded up adaptation of this technology to a variety of metal finishing wastewaters by several years. Of course, reverse osmosis is best utilized to recover and recyle the chemicals from a segregated rinsewater stream and not merely to concentrate the rinsewater to facilitate chemical treatment. Advantages of reverse osmosis are many and will be discussed in another paper at this session. Drawback to date has been the lack of suitable membranes, and our program was concerned with development of those.

SLIDE 4
REVERSE OSMOSIS PROJECTS

Recipient	*Kind of Project*
The State of Minnesota Pollution Control Agency	Survey
AES	Survey
AES	Laboratory (NS-100 membrane)
AES	Laboratory (PBI membrane)
AES	Field Test (Copper Cyanide)
AES	Field Test (Watts Nickel)
AES	Field Test (Zinc Cyanide)
AES	Pilot Plant (New membranes' Evaluation)
AES	Full-scale mobile unit

Fewer projects have been carried out in electrodialysis and other membrane technologies, though all membrane techniques offer similar advantages to R. O. in that they can close the loop on the waste treatment system. Electrodialysis achieves higher concentrations than R.O., and thought is being given to the idea that the two techniques can be combined in sequence, R. O. first and electrodialysis to follow.

Two of our electrodialysis projects are particularly worth mentioning.

Results from the Risdon project, when extrapolated to a full-scale system, promise a payback in about 18 months or less.

Preliminary results from a New Jersey Institute of Technology project shows that electrodialysis, coupled with ion flotation, can provide a closed-loop treatment of fluoborate rinses, which are known to be difficult to treat by conventional methods. What's new here in the technical development is that electrodialysis is used to concentrate an anion instead of a cation and thus promises to provide a practical recovery of costly fluoborate reagent. One result may be more fluoborate plating to replace cyanide, when reliable and simple treatment for fluoborate is available.

We have emphasized advanced treatments for rinsewaters, but we have also looked at some processing solutions and sludges for recovery of materials. Some earlier projects combined plant modifications such as segregation of waste streams and water conservation prior to treatment. Materials were recovered by a variety of techniques. Nickel has been the metal most studied by a variety of recovery techniques.

Particular interest in nickel recovery has been stimulated by high prices of nickel and its compounds. Also, the developers of technologies, as well as EPA, feel that demonstration of metal recovery with a high potential of financial success will encourage use of the technology. And the technology demonstrated for one metal paves

SLIDE 5
ELECTRODIALYSIS PROJECTS

Recipient	*Wastewater Treated*	*Comment*
Risdon Manufacturing	Nickel Rinsewater	Pilot-plant on line
New Jersey Institute of Technology	Fluoborate rinsewater	Laboratory and small pilot-plant on real wastewater

SLIDE 6
NICKEL RECOVERY PROJECTS

Recipient	*Technology*
AES	Reverse Osmosis (Watts Nickel Field Test)
Risdon Manufacturing	Electrodialysis
Seaboard Metal Finishing	Donnan Dialysis
Houdaille Industries, Inc.	Ion-exchange

the way to recovery for other metals. Development of a PA-300 reverse osmosis membrane resistant to both alkali and acids may provide recovery/treatment of zinc cyanide rinsewater and maybe for some chromic acid rinses. Electrodialysis with a suitable membrane may recover hexavalent chromium. DuPont's Nafion® polymer provided a membrane for nickel by Donnan Dialysis and may also work for other metals. Work is being carried out with other polymers to develop new membranes for Donnan Dialysis for a variety of metals.

Evaporation produces pure water and recovers chemicals but is considered to be energy-intensive. Use of evaporation for recovery of water alone and generation of soluble and useless salts for disposal has been criticized as both costly and impractical. However, our two projects, one with a Corning evaporator for recovery of chromic acid, and the second with an Alcoa evaporator for recovery of phosphate cleaning solution revealed that substantial payoff can be achieved. Recovery of chromic acid decreased purchases of new acid by 80% and additional savings came from avoiding chemical treatment for chromium. Alcoa has developed an evaporator that works on waste heat. If a steady source of waste heat is available at the plant, this evaporator can be economically used on a variety of industrial wastes.

Ion exchange is suitable for material recovery and does not concentrate organic impurities. However, chemicals are needed for resin regeneration and there is an effluent stream. Ingenuity in designing ion exchange systems can make some applications very attractive.

SLIDE 7
RECOVERY TECHNIQUES

Evaporation
Ion-Exchange
Cementation
Integrated Treatment
Reverse Osmosis
Other Membrane Techniques
ZDS™ System
(Solvent rinsing system)
Starch Xanthate

Lancy Laboratories invented an ion exchange process based on an "acid retardation" principle, and only water is used for eluting the acid from the resin bed. EPA is demonstrating this technique to recover phosphoric acid used in bright finishing of aluminum.

Another attractive ion exchange system, called Reciprocating Flow Ion Exchange (RFIE), has been developed by Eco-Tec Limited of Toronto for recovery of waste metals from plating operations. EPA is currently demonstrating the Eco-Tec system for recovery of nickel from four rinse systems at the Huntington Division of Houdaille, Industries, Inc. Eco-Tec claims that the economics of their system are favorable, particularly for nickel. If a system recovers 5 kg/hr of nickel salts, payback on capital investment may be as short as 8 months.

We recognize that there are numerous cases where recovery is not at all practical. Therefore we have had several projects on advanced treatment technologies which provided considerable improvements over what was or is available. Let's have a look at the following projects.

Here I would like first to draw your attention to three projects. The first is a sulfide precipitation by insoluble FeS (Sulfex process) that reduces concentrations of heavy metals in effluent to very low levels, works well for mixed metal effluent, and produces easily filterable sludge. There is some concern over safe disposal of sulfide sludges, however, because they may be reoxidized and solubilized.

The second project is the use of ozone as an oxidant for cyanides instead of chlorine or hypochlorite. The main

SLIDE 8
ADVANCED TREATMENT TECHNOLOGIES

Recipient	*Technology*
Beaton & Corbin	Integrated Treatment
New England Plating	Electrolytic
Atomics International	Electrolytic
University of Waterloo	Electrolytic
MFF	Sulfide precipitation
Sealectro Corporation	Ozone
MFF	Activated Carbon and other techniques
MFF	Activated Carbon and other techniques
University of Delaware	Activated Carbon

SLIDE 9
NEW APPROACHES

Recipient	*Kind of Project*
Reed & Barton Silversmith	Feasibility Study of Group Treatment of Multi-Company Plating Wastes
Surface Technology, Inc.	New dielectric surface activation process

advantages are that no hazardous chemicals need to be handled or stored, no dissolved solids are added to the effluent, and the overall cost is comparable with that of chlorination processes.

The third project I would like to mention is the use of activated carbon for a polishing treatment of chromium-containing wastewater. In the case of activated carbon treatment, the pollutants are not recovered, but the carbon must be regenerated to achieve attractive economics. This project, still ongoing, will modify and improve the regeneration of activated carbon.

Centralized waste treatment for metal finishing waste as a private enterprise or as a regional facility has been considered for some time as an alternative approach to individual treatment systems. The users or co-owners, for example, would be small plants located in urban areas, where it is difficult to operate any treatment plant at all. The centralized facility, on the other hand, can be designed and operated to utilize the economy of scale. Our program has made an attempt to explore this approach as a possible alternative route for a small plater. A project awarded to the Reed & Barton Silversmith Co. of Taunton, Massachusetts was a feasibility study of a joint waste treatment plant owned and operated by several companies that generate compatible wastes versus individual treatments by each company. At the end of the study, the companies decided against participating in the joint treatment program, particularly against plant co-ownership. However, the feasibility study is well documented and may convince another grouping of companies to undertake this route.

We also realize that development of new finishing processes which are less polluting than the presently used ones is another approach to minimize environmental problems. We are carrying out one such project, under contract to Surface Technology, Inc. of Princeton, N. J., which is a pilot plant development and demonstration of a new surface activation process needed to prepare a dielectric surface for subsequent electroless copper plating or other types of plating. This process, if successful, will provide an alternative to the commonly used palladium/tin activation process. As I mentioned, palladium is almost entirely imported from the U. S. S. R. The new process will use common metals instead of palladium, require less chemicals, be less polluting, safer to operate and provide a good product. I mention this project as an example of resource conservation rather than of materials recovery.

SLIDE 10
MATERIALS RECOVERED IN EPA PROJECTS

Water
Metals: Ni, Cu, Cr, Zn, Cd
Acids: Phosphoric, Chromic
Anion: Fluoborate
Cleaning Agent: Phosphate

I must admit I have selected very few projects to illustrate today's discussion, and I have highlighted primarily their advantages. For the detailed information about these projects and others which are equally worthy, one should turn to the EPA reports.

However, we all realize that the results obtained in a specific evaluation of an individual technique at a single plant are not necessarily applicable to other plants. On the other hand a failure of technology at a single facility should not discredit this technology without careful examination of the causes for failure.

In other words, EPA-sponsored projects are intended as catalysts from which firms in the industry can develop customized processes uniquely applicable to their own situations by carefully comparing the demonstration work with their own operations, both from a technical and from an economic point of view.

Let's say a few words about the future of R&D.

In general, our R&D program will maintain and even increase its efforts toward development and demonstration of material recovery systems. Needs for research are many and I will mention only a few.

There are wastewaters for which there are no adequate treatments such as effluents with highly complexed cyanide ions, for example. There are not many economic control options for small platers. Reliability of presently used treatment systems can be improved if interferences with chemical reactions are identified and dealt with. In shaping our research program we have been listening to the industry, its associations and its suppliers. We are looking forward to the evening session on the new technology needs.

We have seen in the above discussion that the Federal Pollution Control Act (Public Law 92-500) and local laws and regulations are placing increasingly strict limits on the levels of various substances that can be discharged.

Other factors ranging from the shortage of landfill space to the concern over environmentally safe disposal of wastes limit the options in which waste treatment sludges or untreated effluents can be disposed of. And thus we have seen that the industry is moved towards the only avenue possible, which is materials recovery.

In addition, dwindling natural resources, recent material shortages, and higher materials costs expected in the future are further stimuli to material recovery. We have seen from brief review that the Agency's research projects are mainly oriented toward furthering materials recovery by demonstrating feasibility with such substances as nickel, copper, zinc, chromic acid, phosphoric acid, fluoborate and water.

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Group Treatment of Multicompany Plating Wastes

The Taunton Silver Project

Ms. Marsha Gorden*

OVERVIEW

Perhaps the best way to review and evaluate a project of this nature is to consider the steps through which it has progressed. Thus the total project can be understood in terms of its key variables, permitting duplication as desired.

Step One — Identification of Problem

The concept began at an industrial meeting under the auspices of the regional Section 208 (PL92-500) program at the local Chamber of Commerce. That discussion focused on potential aspects of the pretreatment program that the city soon would be required to implement along with the upgrading of its municipal sewage treatment facility. There was a great deal of uncertainty as to what the specific requirements for the participating industries would be, but there was a general sense of a need for strict metallic limits in order to protect the municipal facility and meet its discharge permit.

Step Two — Consideration of Cost-Effective Solutions

At the conclusion of the meeting, one of the industrialists in particular, who understood the situation, explained that he and the others would need help. Since there were a number of companies in the city with similar product lines and probably similar waste streams, some means of group treatment seemed an appropriate approach to the problem. Subsequent discussions with several of the plant engineers again showed the concern of meeting pretreatment regulations and an interest in a group project. From this start, it was necessary to go to the management levels of the companies next: first, to explain the nature of the coming regulations and, second, to describe a potential group solution.

Step Three — Development of Approach

It was deemed interesting to three companies in particular, which decided to explore the possibility of EPA R&D funding, as there was no precedent for establishment of such a group pretreatment program. Upon selection of an engineering consultant and an institutional subcontractor to accomplish the work, an application was submitted to EPA.

At that time, the three companies signed a "Letter of Intent" indicating their agreement to the overall project and to the designation of one company as "company of record" on the grant application.

The issues of timing and particularly of enforcement schedules became a concern early in the project. July 1977 deadlines were approaching and one nearby company decided not to participate during the initial discussions, believing his permit schedule would not allow a delay. One of the primary three companies was in a similar situation, splitting its effluent between an NPDES permit to the river and the municipal facility. This company elected to stay in the project, recognizing however that most of its waste streams were committed to the scheduled installation and hence not available to group treatment.

Similarly, one of the interested secondary companies in a nearby community was also on a permit schedule and hence not eligible for full consideration. Just before the actual grant acceptance, the other secondary company in a neighboring community was placed on a pretreatment schedule, disallowing its consideration except in a marginal sense. However, the primary three companies continued their participation in the feasibility study as described and divided their costs on a three-way basis.

Step Four — Designation of Common Elements

At the start of the study each of these three plants was analyzed for common characteristics of all batch discharges, including sludges, and of rinse water systems. A chart was drawn up showing alkali cleaners, acids with various metals, cyanides, salvable and inert sludges, hexavalent chromium, and solids. In this way, the three companies' waste materials were compared to determine candidates for group treatment. From this list ten batch wastes suitable for common treatment and disposal were described.

Acids

1. Those high in silver-strips, etchants
2. Those high in copper sulfuric pickles, bright dips
3. Those high in nickel-strips, dragout recovery
4. Those that are relatively low in metal content
5. Those containing hexavalent chromium

Cyanides

6. Those high in silver—filter wash water, floor spill, dragout recovery, strike baths, strips

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7. Those high in copper—same sources as for silver
8. Those low in metal content

Sludges

9. Those resulting from waste treatment which have solids content below 10 per cent solids
10. Those that are untreated—solids removed from the bottom of a process tank, for example

Step Five — Designation of Discharge Points and Disposal Recovery System

Next, the issue of size and location of the companies was considered. Which ones were limited by space and perhaps personnel, and which had access to receiving waters as well as to the municipal sewer? Was there a more centralized location at one plant rather than at another? Discharge to the municipal sewer would limit the project to companies within the city, whereas discharge to a river would limit the size to reasonable transportation distances within the state.

Step Six — Evaluation of Regulatory Procedures

Discharges both to receiving waters and to the municipal sewer would require permits, monitoring and reporting. Similarly, discharge to a hazardous waste landfill would necessitate a permit, monitoring and reporting. There were interactions to be considered and discussed with the EPA regional office, the State Water Pollution Control Agency, and the city department of sewers. The city's sewer ordinance, with its specific metallic limits, was approved by the EPA and the state but still was under review by the local City Council during the progress of the study. It was made available, however, to the three companies and their consultants. The issue of antidegradation on one segment of the river became a concern. All of these regulations and requirements were evaluated as part of the study.

Step Seven — Economic Analysis of Alternatives

The cost-estimating procedure began with individual plant alternatives considering water conservation techniques and various known technologies to meet the different discharge requirements of the river and the municipal sewer. Group alternatives were then developed on the basis of the individual alternatives in order to compare costs. Material recovery proved to be one of the most important elements of the group treatment program.

Step Eight — Evaluation of Institutional/ Financial Elements

Similarly, institutional arrangements were analyzed: who would own the treatment plant(s), how it would be financed, and how it would be operated. The State Department of Commerce and Development was interested in pollution control bonding but was unaware of IRS consideration of material recovery as part of the project. Similarly, local banks were interested in various financial alternatives. There were some new questions to ask, and there were some new decisions to make, but it was institutionally feasible.

Step Nine — Consideration of Potential Project Expansion

The number of companies likely to participate was evaluated in a preliminary manner. With the assistance of the local Chamber of Commerce, a brief questionnaire was distributed to companies having potential waste streams matching the ten batch categories. Interest was expressed on the part of several, but without the city's proclamation of the sewer ordinance with its metallic limits, companies were hesitant to release specific information. Many were not even aware of the upcoming sewer ordinance and their potential pollutants to the municipal sewer.

Step Ten — Final Analysis of Alternatives and Decisions

At the completion of the study, the three companies had received much data—technical, regulatory, financial and institutional. They are presently evaluating all this information in order to make required decisions. It is anticipated that the municipal sewer ordinance will be released shortly with a compliance schedule, thus providing a citywide focus on this project.

INTRODUCTION

Objective

This project has been designed to test the feasibility of bringing together and treating common wastewater streams from three manufacturers of silver and silver-plated holloware. In particular, the study has been planned to explore alternative group industrial wastewater treatment technologies applicable to this segment of the electroplating industry for three basic purposes:

- To determine the potential for cost savings with group treatment,
- To develop the legal and institutional arrangements necessary for group treatment implementation, and
- To encourage opportunities for material recovery and industrial water reuse.

A project of this nature can demonstrate the opportunities for aggregating materials within a region to accomplish environmental goals at reduced costs.

The issue of economy of scale for this industry made up of many small companies has never been demonstrated in a group project of this nature. Accordingly, this study has been designed to develop the technical/institutional/financial factors necessary to evaluate group and individual treatment alternatives. If the problems were viewed only from the treatment perspective, its utility as an example would be limited. However, by incorporating the legal, institutional and reuse components, a more complete view of the industry problem is presented. By including these components, the solution is of value to Taunton as well as to others looking for answers to similar problems.

It should be recognized, however, that any example is a unique combination in terms of size, product, associated waste streams, and nearby disposal opportunities.

Consequently, this project should be viewed not as strictly typical of this industry or the region but rather as an example presenting a group of variables and circumstances which are useful as a model. In this way, the report can be read as a demonstration of an evaluative approach and thus can be more useful to a larger audience.

Project History

This project was an outgrowth of a Section 208 (PL92-500) areawide wastewater management plan under development by the Southeastern Regional Planning and Economic Development District (SRPEDD) of Massachusetts. In the course of investigating the impact of industrial wastewater discharges, it became apparent that opportunities existed for joint treatment of similar industrial waste streams in the study area. Analysis of industrial effluents in the several river basins under SRPEDD's planning jurisdiction indicated similar waste streams in proximity to each other, particularly in the City of Taunton.

This city has a long history of metal crafting beginning with America's first ironworks in 1656. From that start the city has favored industry rather than agriculture, building a tradition of metalworking which, today, takes the form of silverware, bronze and copperware, stainless steel, pewterware, and other metallic items. Many of the present-day companies employ electroplating processes that, as a group, release a variety of metals to the Taunton River, either through direct discharge or through the municipal treatment plant.

The Companies

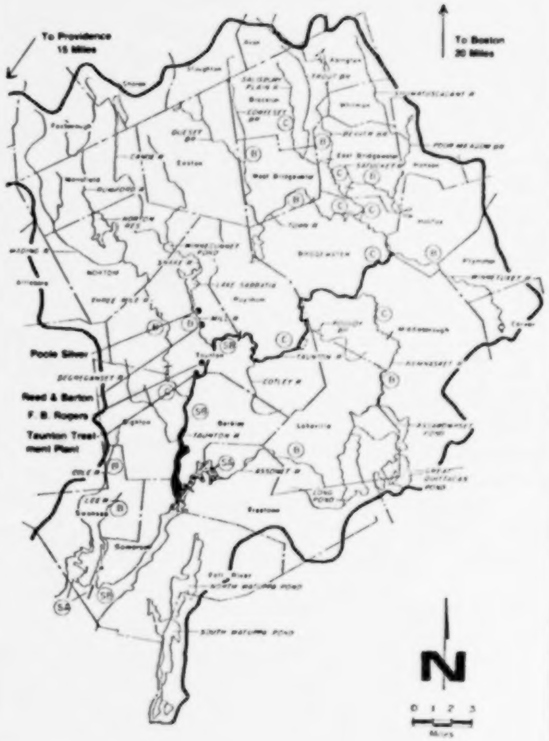
The three companies participating in this project represent an extension of Colonial America's early tradition of metal craft, which included silver-smithing. Reed & Barton, founded in 1824, is one of the country's oldest and largest silverware manufacturers, presently producing a varied product line of tableware and holloware. Poole Silver Company, a Division of Towle Manufacturing Company of Newburyport, Massachusetts, has been in Taunton since 1893 and produces silver-plated and pewter holloware. These two companies are located on the Mill River, a tributary of the Taunton, as shown in Figure 1, "Classification Map of Taunton River Basin." F. B. Rogers Silver Company, a wholly-owned subsidiary of National Silver Industries, Inc., is located directly on the Taunton River where it has a long history of producing silverplated and pewter holloware. Detailed descriptions of the plants are available in the complete report.

The Community

During the period of this project, the City of Taunton, with its Conservation Commission, has begun a Riverbank Beautification Program. With the assistance of the Comprehensive Employment Training Act (CETA) employees, initial steps to clear sites for walking and cross-country running have been taken. The preliminary plans call for additional land acquisition and future work to provide foot-bridges over the river, a bicycle path and a boat landing.* Since most of the Taunton River has already been identified and now is charted as a Wampanoag Indian Canoe Passage** across southeastern Massachusetts, there is additional interest in the river's past uses for transportation and fishing.

The completion of an industrial pretreatment program such as this report describes along with the upgrading of the municipal sewage treatment plant will encourage these additional activities along the river in accordance with the water quality goals previously established.

Figure 1
Classification Map
Of Taunton River Basin



*Source:
The Taunton River Basin, Part A Water Quality Data
Department of Environmental Quality Engineering Commonwealth of Massachusetts, Division of Water Pollution Control, Westborough, Massachusetts, December 1975.

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* Further information available from the Taunton Conservation Commission, P. O. Box 247, Taunton, MA 02780.

**"Wampanoag Commemorative Canoe Passage," prepared by Plymouth County Development Council in cooperation with the Bristol County Development Council.

TECHNICAL ASSESSMENT

The technical assessment required to meet the objectives of the study includes:

- Analysis of the pollution control problems facing the three firms, including the mutual problems caused by manufacturing operations, the unique problems presented by their location, and the physical statistics relative to each firm;
- The treatability of the process wastewater;
- The various concepts employed in development of a multicompany treatment facility.

The technical assessment provides the basis for the various economic considerations presented later in this report. Detailed information relative to each firm and potential group treatment is provided in Appendices A through D of the complete report.*

Pollution Control Problems

All three firms are large producers of silverplated holloware. As one would suspect, the basic steps required to produce silverplated holloware from brass sheet stock result in many common wet process operations that produce similar wastewater. Obviously their location in Taunton, Massachusetts, presents each firm with common problems relative to meeting regulatory requirements. Many of the pollution control problems are unique to this location. This is important to understand when using the information in this report. In order to consider the concept of multicompany treatment of plating wastes for other areas, a description of each participating firm and its particular pollution problem is provided. These problems are subdivided into discrete problems, such as wastewater streams that are common to all three firms as well as unique to each one.

Common Features

Manufacturing Operations—
In the production of holloware, brass sheet stock is mechanically pressed into shapes which are then soldered to each other. The various decorative edgings, legs, handles, etc. are next soldered to items to produce the final shape of the finished part. Prior to plating, the assembled parts are polished and buffed to obtain a highly reflective surface for finishing operations. The assembled parts are silverplated using cyanide solutions. In some cases an underplate of copper and/or nickel is employed. After plating, a final finishing operation is used to mechanically produce a product that is uniform in appearance.

Wet Processing—
The most common wet processing of parts is cleaning. Depending upon the particular production item, a given piece of metal may be cleaned as many as seven times from start to finish. Cleaning is employed in stamping and drawing steps, before and after annealing, before and after solder assembly, after polishing and buffing, prior to plating, and in some cases during final finishing. The alkaline cleaners used in these steps have been selected to result in minimum attack on the base metal.

Strong acids are employed to remove annealing scales. However, the majority of acids used are only mildly corrosive to the base metal in order to maintain the appropriate surface finish. All firms employ either fluoboric acid or proprietary mild acid salts for surface activation prior to plating to minimize attack on the polished base metal and to satisfy the demands of the tin-lead alloys used for decorative and assembly objectives.

Cyanide copper plating is used to cover the parts with an initial plate, enhancing the adhesion of subsequent electrodeposits. Conventional acid nickel is plated onto some parts, either as a final finish or as a preplate prior to silver. Silverplating is done in conventional cyanide solutions using proprietary brighteners. Attempts to replace cyanide solutions with plating baths free of cyanide have not been successful.

As is common to other plating operations, a modest percentage of wastewater results from chemical stripping of plating fixtures, or racks, and the stripping of items for rework and salvage.

Combined Wastewater—
Another common feature for these three firms, which is not unique for older plants that were built and were expanded when concern for pollution control was minimal, is presented by the multiplicity of drain systems that combined process water with cooling water and sanitary wastewater. When these plants were built, the only concern appeared to be to remove all water from the plant. Wet processing is scattered throughout the plants and located to optimize material flow and is not located to centralize the wet processes—or their wastewater.

Water Waste—
Another common feature for these three firms is the excessive use of water. When the cost of water was the only concern, and as it was initially a cheap commodity, production lines and plating practices were established wherein large quantities of water were employed in rinsing and cooling water applications. Excluding water used for sanitary purposes, the three firms used a total of 425,000 gallons per day. With the concern for water conservation, changes in the past several years have reduced this water consumption somewhat. Now, with the objective of minimizing water pollution control costs, further conservation effort became mandatory. An estimated reduction of 280,000 gallons per day can be realized for these three firms as they act upon recommendations.

Silver Reclamation—
As the value of silver has risen over the years, various efforts have been implemented by the three companies to minimize their losses to the sewer. The attention directed

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*The report will be available from the Industrial Environmental Research Laboratory, EPA, Cincinnati, Ohio 45268.

to these silver reclamation efforts naturally depended upon the quantity being discharged. For many years, spent process solutions that were high in silver content were shipped out for reclamation of silver values. In one case, where efforts to control pollution were initiated in 1972, silver reclamation was extended to include the sludges resulting from cyanide oxidation. At another firm, treatment of some rinses with metallic zinc to displace dissolved silver by cementation allowed for partial recovery of silver draining to the sewer. All firms have recently adopted electrolysis as a means of lowering the silver content in dragout recovery tanks—and thus reducing the amount of silver entering the rinse waters. When the pollution problems are resolved, recovery of additional silver can be realized.

Wastewater Characterization—

The final common feature of the pollution control problem relates to the process water itself. All firms have water that can be segregated into:

- Waters resulting from alkaline cleaning which are mildly alkaline and low in heavy metals;
- Waters that are acidic and/or alkaline in nature which contain minor amounts of the heavy metals—copper, zinc, tin, lead and nickel (only two of three for nickel);
- Waters that are strongly acidic and contain high concentrations of heavy metals;
- Cyanide-bearing water that invariably contains copper and silver; and

additionally, in two of the firms there are waters that essentially contain only suspended solids. Also, wastewater contamination levels increase significantly when spent or contaminated process solutions are dumped into the sewer.

The Three Companies

Company A has been discharging during a single shift operation in excess of 220,000 GPD of industrial-use water, through seven sanitary sewer outlets, with all but one being combined with sanitary wastewater. Water is used in thirty departments located in twelve buildings. A significant problem is presented in the isolation and collection for treatment from these sources. The problem is compounded by the need to segregate the wastes for treatability purposes and magnified by the river dividing the plant in half. The process wastewater contains objectionable amounts of cyanide (including complexes of copper and silver) and the heavy metals copper, zinc, silver, nickel and iron. Lesser amounts of chromium, tin and lead are present, which will become of concern as water conservation efforts eliminate the dilution effect. Historically, the wastewater has been acidic. With the preponderance of alkaline cleaning and a minimum of acid processing, it would be expected that the wastewater would be near neutral or slightly alkaline. It is believed the acidic condition is as much a result of the quality of the raw water as it is of the metal finishing and plating processes employed.

Company B has been discharging during a single shift operation in excess of 33,000 GPD of industrial-use water combined with additional sanitary wastewater. The collection, isolation, and segregation problems are not as complex as at Company A, but it has no land available for expansion to install treatment facilities and will have to use a storm sewer if discharging to the river.

Company C has been discharging during a single shift operation in excess of 130,000 GPD, with 40,000 GPD entering the Taunton River under an NPDES permit and the rest via three connections to the sanitary sewer, two of which are mixed with sanitary wastewater. Unlike the other two firms, this company has been treating wastewater discharging to the river and pretreating most of its wastewater discharging to the sanitary sewer. As with Company B, this firm has no adjacent land to use for additional treatment facilities. The untreated process wastewater contains objectionable amounts of cyanide (including complexes of copper and silver) and the heavy metals copper, zinc, silver and nickel. Lesser amounts of tin and lead are present. The most pressing problem facing this company is the necessity to upgrade its existing treatment facilities in facing the more exacting limits established by new regulations.

Concepts

The concepts considered under this study include each firm treating its own wastewater; group treatment of combined wastewater, in total or in part; and extension of group treatment facilities to include other firms having similar wastewater. In addition, considerations have been given for recovery values for salvable metals, techniques for enhancing the values as volume expansion permits, and new technology having potential merit.

Detailed descriptions of facilities for each plant are provided in Appendices A, B and C of the complete report. Those identified as Primary Design consider each plant being required to treat its own waste separately and form the basis for comparison of alternatives. In addition, the impact caused by discharge point (sanitary sewer vs. stream) is described. The advantages of reusing treated process water are brought forth. A description of joint efforts is provided in Appendix D of the complete report. In considering expansion of group treatment effort, some alternatives discussed for the companies include concentration of rinse waters.

Assessment

From an overall viewpoint it appears that the best interest of the firms and the total environment will be served by each plant treating its own flowing rinse waters and by combining the firm's efforts for treatment of the batch wastes resulting from the dumping of spent process solutions, from accidental discharges, and waste treatment operation resident for each plant. Additional benefits can be gained by concentration of selected rinses for subsequent batch treatment. The values for salvable metals are improved by the group venture's use of more efficient technology.

The advantages of group treatment that will influence any decision to proceed include:

1. Cost reductions will result from bulk purchases of treatment chemicals that would not otherwise be available for each firm acting independently.
2. More efficient sludge handling facilities can be applied for all firms with a reduction in disposal costs anticipated.
3. Batch treatment equipment will receive greater utilization by expanded capacity, resulting in a lower cost per unit treated.
4. Technicians will expend a greater portion of their time on batch wastes and, in doing so, will become more skilled, thus enhancing environmental quality.
5. The extramural support (analysis, assay, consultation) for the single facility will be less than were each treated separately.
6. The net salvage values received from refiners for silver, after deducting processing costs, will be higher.
7. Salvage potentials for copper and nickel become more practical as the amount involved increases by multiple company efforts.
8. More efficient reclamation methods can be justified by joint action than for each independently. The potential for separating copper and silver from mixed cyanides carries with it certain development expenses that can be amortized over expanded use.
9. Electrolysis of concentrated cyanide solutions as proposed for the group treatment is approximately 15 - 20 per cent of the operating cost required by chlorination. This capital intense process requires a minimum quantity of batch cyanide wastewater to justify the greater cost to buy and install than existing with chlorination techniques.
10. As the problems relating to solid waste disposal become resolved, costs will escalate. Disposal in bulk will reduce expenses to all firms.

It can be concluded that both the environment and the firms involved themselves will benefit from group treatment of batch wastewaters. The information on the economics to support this conclusion follows in the next section.

ECONOMIC ASSESSMENT

The assessment of economic considerations included the capital investment and operating expenses for: each plant providing its own complete wastewater treatment facilities with multiple discharge points; various alternatives for each company; group treatment of the three companies' wastewaters; expansion of the group treatment concept to include other firms; and recovery values. The data summarized in this section are explained in detail in Appendixes A through D in the complete report.

Two economic factors have not been included in this assessment. Depreciation of equipment depends upon judgment factors and upon tax incentives. The other economic factor applies to the concept of "cost of money," wherein annual expenses are attributed to having one's capital tied up in nonproductive facilities. At the present time, the "cost of money" is in the 8 to 10 per cent range. The reader is left to apply these two factors to annual operating expenses as desired.

Three Separate Facilities

As a basis for comparison of alternatives and potential joint treatment of wastewater, the following data are presented for each firm. Included for Companies A and B are the economic impacts of not being able to use the river for discharge of part of their treated wastewater; then total discharge would be required to the sanitary sewer. The economic advisability of reusing treated wastewater has also been estimated.

Company A

The Primary Design—using complete treatment of some rinse waters prior to stream discharge and pretreatment of other rinse waters prior to discharge to the sanitary sewer, together with batch treatment—will require a capital investment of $640,500 and result in an annual operating expense of $138,595. A modest reduction in operating expense will result from partial reuse of treated waters. If stream discharge is prohibited, expenditures increase by 15.8 per cent for capital and 27.8 per cent for operations. Under the total discharge to the sanitary sewer concept, the savings by reuse of treated water are much greater and show a 13-month return for additional invested capital required for reuse of the treated water.

The data shown for the design that considers elimination of batch treatment facilities may be misleading if used out of context and compared with subsequent information concerning group treatment. Certain discrete components would be required for rinse water treatment which might be used also for batch treatment. Since their common use is practical at a common treatment site, the capitalization and operating expense should not be duplicated, but rather prorated as to use by each company. Caution must also be expressed for the somewhat small increase in operating expense when comparing this alternative with the Primary Design. The costs for contract hauling and disposal reflect present economics. As the regulations governing this cost become fully developed, it is believed that the disposal costs will increase drastically as the cost of disposal is passed back to the generating source. One source questioned anticipates a 1000 per cent increase over current rates.

Company B

As with the previous firm, the most attractive alternative considered a dual discharge (i.e. stream and sanitary sewer). This Primary Design is expected to require a capital investment of $141,000 and result in an annual operating expense of $37,977. If stream discharge is prohibited, expenditures will increase by 13.7 per cent for capital and 34.0 per cent for operating expense. Again, reuse of treated water is advisable—although the rate of return for additional invested capital is lower than for the previous firm, as the potential for cost reduction is smaller with only a portion of the available water being reused.

As with the previous company, the concept that eliminates batch treatment contains the same probability for escalated disposal costs for collected batch wastes. At Company A some of the equipment used for treating rinses finds utilization in batch treatment. However, for this smaller Company B, transfer of batch treatment operations to another location does not significantly reduce capital investment (less than 5 per cent reduction).

This company is presented with an option to replace a segment of its rinse water treatment system with evaporative recovery. There is little difference in capital investment. Operating expenses increase approximately 10 per cent—primarily because of higher energy requirements.

Company C

This company has completed its capital investment for a major portion of the waste treatment facility during the past three to four years. The capital values shown are what one would expect to invest at today's market conditions and do not necessarily reflect actual expenditures in the past. In addition, certain unique conditions that caused higher than normal expenses have not been included so that the overall picture will be more representative of the average plant yet to face its pollution problem entirely. (For example, with normal high tide in the adjacent Taunton River being 12 to 18 inches below the plating room floor level, high expenses were realized in installing five-foot deep sumps used to collect wastewaters.)

The design approach employed for the Primary Design was similar to that used for the other two firms, except that it was influenced by earlier design concepts that resulted in the existing facilities. Since the present river discharge is being influenced by the existing upgrade efforts, it was felt that initially little attention should be directed toward increasing the facilities used for river discharge. As a result, the Primary Design is not considered to be the most attractive alternative. Alternative 1 shows a modest (1.7 per cent) increase in capital expenditure which is returned the first year through reduced operating expense. By being located adjacent to the Taunton River, this company does not have to consider final filtration at the same time as the other two firms.

Under Alternative Design 1 a greater portion of the wastewater containing heavy metals is diverted to the river discharge. Capital expenditures are valued at $299,500 and an annual operating expense of $49,888 is expected. Using this concept, little economic advantage is realized through reuse of treated process water.

Again, the design that uses contract hauling in place of batch neutralization is factored for disposal costs that are not expected to remain at the present price. Much of the batch treatment equipment required for complete in-plant treatment is already installed. Consequently, the opportunity for reducing capital costs is lower for this firm. The greatest advantage to this company of using group treatment facilities will come from reduced operating expenses and improved silver recovery.

Group Treatment

The economic assessment for group treatment efforts considers that each plant will install its own treatment facilities for flowing rinses and that batch wastes will be treated at Company A. It is not practical within the scope of this study to factor all the possible permutations presented by the various alternatives. Rather, the most practical combinations, and those that are most likely to occur, are used for the economic assessment of group treatment.

For the purposes of quantifying the various cost factors, that portion of Company A's facilities used for batch treatment is identified as though the group treatment facilities were a fourth identity. Those items that are used by both rinse water treatment and batch treatment have been prorated to each system as an aid to quantifying this option.

Capital Expenditures

The capital expenditures listed consider that each firm will treat its own flowing rinse waters at its respective plant; that collection facilities will be provided for segregated batch wastewater and residual wastes from their treatment facilities; that stream discharge will be permitted for each firm; that there will be maximum utilization of treated wastewater; and that batch wastes will be treated at Company A.

With the same four capital factors as used previously, the capital expenditures for each company to treat its rinse waters will be:

Company A	$484,500
Company B	$141,600
Company C	$293,300

with the joint batch treatment facilities being located at Company A

Joint Treatment Facilities	$173,900.

The total capital expenditure amounts to $1,093,300 and should be compared with the capital required for each company to install its own complete facilities ($1,096,000). Within the accuracy of cost analysis, these two figures indicate that there is no capital advantage one way or the other.

Operating Costs

Using the same basis as applied for capital expenditures, the annual operating expenses will be:

Company A	$100,900
Company B	$ 31,900
Company C	$ 44,300
Joint Treatment Facilities	$ 41,300

Comparing this with the expenses anticipated at each plant if totally treating its own waste, a modest saving of $3,000 per year is expected. This does not include depreciation of equipment and the cost of borrowing, as previously discussed.

Cost Variations

The various cost reductions listed in the earlier section which result in group treatment efforts for batch waste reductions can be quantified.

Sodium hydroxide, in bulk shipments, will cost approximately 50 per cent of the price in drum lots.

Sludge disposal rates will gain by bulk shipments, which are prices at $0.13 per gallon versus $0.40 per gallon in drum lots. It is also expected that the volume of sludge will be reduced by the more sophisticated handling facilities. Sludges with a solids content of 20 to 25 per cent will result, as compared with 5 to 7 per cent. This will result in approximately one fourth the amount requiring disposal.

Greater utilization of equipment used for batch treatment will reduce cost factors of equipment depreciation as applied, for each gallon treated will be approximately 50 per cent. Extramural support will be reduced by approximately $4,000 per year. This primarily related to insuring quality of sludges. Other cost variations relative to reclamation are discussed later in this section of the report. Cost increases will result from transportation and these costs are budgeted at $3,000 per year.

Expansion

The expansion of group treatment efforts will depend upon normal market conditions. Major costs are attributed to the treatment of flowing rinse waters, with far less capital involved in treating batch wastes. Company B is a good illustration when considering expansion of group treatment to include other companies. The opportunity of reducing capital costs will exist; reduced operating expenses can also result. It is not practical under the scope of this study to quantify group treatment expansion in more than the broadest sense.

Expansion is possible without any increase in capital investment. The facilities included in the joint batch waste treatment operations are not used 100 per cent of the time. The various subsystems have been sized to maximize labor use. This results in some of the equipment being underutilized. As the amount of batch waste to be treated is expanded, only the direct expenses of labor, energy, chemicals, supplies and sludge disposal will increase. When the cost factors that consider applied overhead and depreciation of equipment are prorated across each individual batch being treated, then the cost per batch will decrease according to the total volume under any expansion concept.

The facilities considered to be a minimum for the three firms as described earlier have built-in expansion factors of 40 percent for batch acids, 20 percent for batch cyanides, and 80 percent for metal reclamation before any additional capital investment is required—other than larger storage facilities for raw waste.

Recovery Values

The previous assessment of economic conditions does not show an overwhelming advantage of group treatment to produce acceptable water and sludge discharges to the environment. Attention has been focused on pollution control itself. Cost advantages do exist relative to the discharge of residual sludges resulting from waste treatment practices. Where recovery of metal values exists, a decided advantage can result from use of more sophisticated facilities than can be justified for only the large plants. In the case of the three firms involved in this project, the primary consideration for metal recovery is silver. If the volume increases, copper and nickel should be considered.

Silver reclamation for these companies is extensive. Particulate matter removed from dust collection systems is shipped out to our refiners for reclamation. Some solutions known to be high in silver are returned to vendors for reclamation. Metal scrap is salvaged for silver content. Additional salvage values will result from processing waste treatment residuals.

Two other metals, copper and nickel, have potentials for salvage should the volume become larger through expanded use at the treatment facility. At today's prices, nickel will bring $1.76/kg ($0.80/lb) in solution form and $0.77/kg ($0.35/lb) in sludges. These values will be reduced by the costs of shipment and should be considered only when concentrations are high enough and volumes warrant bulk transportation. Copper in solution form can bring $0.88/kg ($0.40/lb), subject to the same conditions.

Assessment Summary

As discussed earlier, when considering waste treatment costs to resolve environmental pollution problems alone, significant dollars are involved. For these three companies, there appear to be marginal advantages to group treatment of process wastes. However, when including the recovery values for reclaimable metals, the annual operating expense is reduced from $218,000 to $88,000. The full cost reduction can be realized by group treatment. It is believed that the added expense to each firm to implement individually the recovery aspects will consume at least half of these savings.

In the introduction to this section, two economic factors were excluded—depreciation and "cost of money." To fully appreciate the advantage of increased utilization when applied to the batch treatment system, these factors should be included. Assuming ten-year useful life for equipment, the depreciation on a straight-line basis for the group treatment facilities is $17,390 per year. At an 8 per cent "cost of money," an additional $13,912 per year is processed. If spread evenly, this will amount to approximately $0.16 per gallon of waste processed. All other operating expenses for the group batch facility have been listed at $41,300, or $0.21 per gallon processed. The total is $0.37 per gallon. Obviously, some process solutions require a higher share of these costs than others, but averages can show the advantage of greater utilization. Depreciation and "cost of money" represent 43 per cent of the treatment expense with maximum utilization by these three firms. With less use, as caused by each providing its own batch treatment facilities, this 43 per cent expense climbs. By a similar consideration, increased utilization is possible by expanding the joint facility to include other firms, which will result in a lowering of this cost per gallon from $0.16 per gallon to less than $0.10 per gallon.

In spite of the variable cost factors evaluated in this chapter, group treatment does have an advantage when metal recovery economics are considered and disadvantages related to individual company treatment operation are fully appreciated.

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Development Sciences Inc. (DSI) of Sagamore, Massachusetts, provided the overall study approach. Additionally, DSI identified the institutional and financial factors associated with ownership and operation of the group treatment alternatives and prepared the final report. Ms. Marsha Gorden of DSI served in a coordinating capacity among the participating groups.

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The Electrochemical Removal of Trace Metals For Metal Wastes with Simultaneous Cyanide Destruction

By I. F. T. Kennedy & Dr. S. Das Gupta*

INTRODUCTION

The plethora of problems facing the metal finishing industry in the area of pollution control stem from the private and public desire to improve our environment. It is not a question of whether or not there should be control of industrial pollution, but rather the how, with what, at what cost and by whom.

The metal finishing industry is subject to at least three levels of regulations concerning the discharge of liquid effluents. These are: Federal, under The Pollution Control Act Amendments; State, as enacted; and Municipal, where applicable. Further, the industry is or soon will be, regulated with respect to the disposal of solid wastes.

The Pollution Control Act Amendments (Public Law 92-500) enacted by Congress in 1972, has as its essence the cleaning up of the lakes, streams, and oceans of the United States and to achieve essentially a zero discharge of pollutants into the Nation's waterways by 1985.

The Environmental Protection Agency was charged with the herculian responsibility of carrying out this expression of the public's will. The mandate requires the establishment of wastewater effluent limitations to be achieved by all industrial operations whose activities result in the release of toxic substances into surface water.

The history of the promulgation of limits for the electroplating and metal finishing [illegible] is not at issue here, but rather the practical problems facing the industry as a result of these limits. The industry must remember that the EPA has a public responsibility to enact and enforce in order to fulfill its charge. Industry's problem has been the practical solution as to how to meet the limits being legislated.

I am sure that many of the principal waste treatment technologies currently available to industry will be exhaustively reviewed elsewhere at this conference and it is therefore the intention of this paper to focus initially on the rationalization of the existing metal finishing plant and on the improvement of existing plant practices and thereafter to detail a new electrochemical system currently being developed as an advanced pollution control system.

The Metal Finishing Industry

The scope of the problem of pollution from the metal finishing industry in the United States is reflected in the size of the industry and the quality and complexity of the effluents being discharged.

The electroplating and metal finishing industry in the United States is large and complex. The strategic importance of the industry cannot be underestimated; indeed I doubt there are many industries which, if forced to cease production, could as effectively cripple the industrial productivity and capacity of the United States. The National Association of Metal Finishers estimate that they are in direct contact with more than 7,000 electroplating and metal finishing facilities and that the true number may be as much as three times that figure.

The geographical distribution of known facilities closely follows that of heavy industry in the United States. The heaviest concentrations are in the North Central Region which account for nearly 40% of known facilities, followed by the Atlantic Coast States with 35%, the West Coast, and particularly California, with 6%, with the final 20% being distributed throughout the remainder of the country.

This geographical distribution indicates the close relationship between the metal finishing shop and the source of the work piece processed. This leads to intense price competition between plating shops and, in general, metal finishing industry profits are measured in cents or fractions of cents per work piece. It is therefore readily evident that management in this industry must be intensely cost and price conscious in order to simply stay in business. Pollution control equipment is generally viewed as a capitally intensive, non-productive item requiring an excess of floor area in an industry where work space is at a premium. To date, pollution control equipment has been regarded by management as an unwanted expense and there has been little or no economic incentive to install such equipment. Further, most metal finishing shops are small to medium in size, non-integrated or affiliated, owner-operated, without the in-depth knowledge of waste treatment technology to facilitate decision making and lacking in readily available capital necessary for the purchase and installation of such equipment. These factors have manifested themselves in the resistance of the industry to pollution control measures and

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are further reflected by the uncertainties expressed frequently by industry's management, i.e. "whom do I trust to tell me what to do, where do I obtain the capital for this system, and after all of this, will the system as installed meet the E.P.A. limits".

While readily acknowledging that the answers to these questions are neither simple nor immediately available, we at H.S.A. believe that the resolution often lies in the asking of the right questions. Usually management itself is quite capable of determining which is the best course of action after it has carefully and systematically reviewed the questions.

It is also important to note that more than 52% of all electroplating and metal finishing establishments are located in cities have a population greater than 100,000 and more than three-quarters of the plants are located in cities with a population greater than 20,000. The distribution cited above would favour such waste disposal practices as sewering of liquid wastes (with or without treatment and solids separation) and off-site disposal of non-sewerable waste, utilizing contractor services. A sampling of facilities conducted by Battelle Columbus Laboratories and reported in 1976 indicated that waste treatment equipment for chemical in-line and end-of-line waste water control is generally less than five years old, although some equipment in a few cases had been utilized for about twenty-five years.

Metal Finishing Industry Effluents

The toxic and metallic contaminants in the waste effluents from the electroplating and metal finishing shops simplistically derive from the work pieces being plated, the chemicals and solutions additives used in the plating process, and from the deterioration of the plating plant equipment. The contamination from the work piece may be of the oils and greases scale or from the dissolution of the work piece during the surface preparation. The contamination from the plating solutions and chemical additives is self-explanatory and the contamination from the plating equipment may be dissolution of anodes of unprotecting plating tanks or of the pipes carrying process solutions from one place to another within the plant.

The principal source of metallic and toxic chemical contaminants in a plating plant are the rinse waters from each plating step which are dragged out from concentrating solutions. Also included are process solutions such as alkaline cleaners, acid dips and pickles and conversion coating solutions some of which are dumped by some plants at regular intervals. The conventional water pollution control practice in electroplating and metal finishing facilities involves the precipitation of the dissolved potentially hazardous toxic materials, thus generating a sludge destined for land disposal.

Rinse waters commonly contain alkalies, acid with dissolved metals, and possibly cyanides. The metal or metals being plated on to the work pieces appear as dissolved salts in the rinse waters following metal deposition steps. Supporting electrolytes and additives introduced to enhance electro-deposition of the deposit may also be present. Some plating processes incorporate post-plating steps intended to alter the metal surfaces by conversion or filming to improve on the corrosion properties of the metal deposits. Dragouts from these solutions also contain metals and chemicals. Normally the rinse waters from a plant are collected into three distinctive streams. One carrying all cyanide-bearing wastes, another all the chromium-bearing wastes, and a third containing all alkalies and acids and metal salt solutions other than chromium and those metals which are chemically bound to cyanide. The chemicals are destroyed or reduced by treatment in a water pollution control system, metals are precipitated and separated generating sludges, and the effluent is discharged to a stream or sewer.

Pollution Control Technology

The range of pollution control technology currently available to industry mirrors the range of effluents described above.

The principal technologies currently available are all physio-chemical methods and include:

a) Conventional chemical-destruct methods including chlorination and hydroxide precipitation;
b) Ion exchange;
c) Dialysis and electrodialysis;
d) Evaporation;
e) Reverse osmosis;
f) Carbon adsorption and catalytic and chemical oxidation;
g) Miscellaneous methods such as freezing, ion flotation, liquid liquid-extraction, and ultrafiltration;
h) Electrolytic methods.

This list is illustrative of the different directions from which the pollution problems are being attacked.

This list further illustrates that since management must live with its decisions, it is essential that management is instrumental in making these decisions. Only when management has a thorough understanding of the specific problem areas within its own plant can an evaluation be made of the advantages and disadvantages of the alternative solutions available in pollution control.

PLANT ASSESSMENT SURVEYS

Survey Purpose and Method

In view of the range of alternatives available to management in pollution control technology we believe that the examination and particularly the installation of a pollution control device is a waste of capital and management's time if considered in isolation. The entire metal finishing plant, with all its sequence of unit operations and its existing plant practice must be considered as a total before determining the best approach to pollution control equipment and practice. Our approach has been to review the plant as it exists today, ask management its objectives and work with management in achieving those goals by rationalizing existing facilities and plant practice and suggesting any necessary changes, additions or deletions.

The purpose of a plant assessment survey for pollution control is to: analyze current plant physical layout, operating practices and procedures and recommend any changes in equipment or practice which would result in lower contamination levels in the final effluent discharge; examine process water usage and recommend methods of reduction; evaluate the efficiency and effectiveness of any existing pollution control equipment or waste treatment facilities; recommend any changes or additions in instrumentation or equipment with respect to existing pollution control or waste treatment equipment which would improve the discharge quality.

The plant assessment survey focuses on the collection of data, including updating of plant layout, piping and flow diagrams, arrangement and relationship of plating lines, the initiation of a program of chemical analysis of all plating baths and rinse tanks, the analysis of the material and water balances in order to assess the effectiveness of the existing plant practice, to suggest to management methods to reduce the metallic contaminants in their final discharges and to improve the process water usages. This logical approach utilizes sound scientific and engineering principles and permits management to study their own plant in depth and in an organized and rational manner. By way of example, I would like to indicate what has been accomplished in one plant by progressive management.

Assessment Survey Example

Introduction

The metal finishing plant illustrated here is an existing operation and is typical of the majority of plating operations utilizing a full service approach with automatic chrome rack and zinc barrel lines as well as hand lines for the plating of zinc, copper, nickel, cadmium and lead and, occasionally, gold. This plant did not happen to include such plating processes as phosphating, anodizing, mechanical plating, electroless nickel or dye operations. However, the assessment survey approach would be exactly the same for plants with these types of plating facilities.

Figure 1 (Slide No. 1) indicates the physical equipment and piping details as well as the materials and flow balance in an existing plant. This diagram, although not strictly to scale, is proportional. It indicates that the plant layout fits the work flow extremely well. The most striking feature is the huge size and the floor space requirements of the installed Waste Treatment Facility. This unit occupies nearly 25% of the floor area of the entire plant and approximately equals the floor space allocated to the productive plating lines.

Analysis of Existing Waste Treatment Facility (WTF)

In order to assess the efficiency of the existing alkali-hypochloride chemical destruction waste treatment facility, a programme of daily analysis of the final discharge was carried out over a period of five weeks. The statistical mean of the concentrations of various constituent contaminants in this effluent is given in Table I (Slide No. 2).

From Table I, it can be generally concluded, that the chemical destruction process applied to the plant discharge was as effective as could be expected in reducing the metallic and cyanide levels in the final effluent. The table illustrates that the system is quite effective in percentage removal when initial concentrations of contaminants are high and considerably less efficient when the initial concentrations are low. The use of an in/out ratio removes the impact of dilution but points out that the higher the dilution (i.e. the more unnecessary process water utilized), the more dilute the streams entering the WTF will be, and the lower the percentage removal will be (i.e. the WTF is less efficient).

All instrumentation was checked for proper location in the unit and for accuracy and calibration. The physical retention times in various tanks were checked against various chemical reaction rates to ensure that there was ample time for the completion of all chemical reactions in the destruction process. It was concluded that sufficient time was being allowed for the oxidation of the cyanides to cyanates and the subsequent hydrolysis reactions.

It was our conclusion that the Waste Treatment Facility in isolation was as efficient as could be expected for a chemical destruction facility of this type; that the instrumentation controlling the destruction process was adequate and functioning normally; and that there was sufficient retention time for the appropriate chemical reactions to go to completion. It is also evident that the facility principally treats zinc, iron and cyanides.

Analysis of Rinse Tank Discharges & Plant Operation Practices

The second stage of the Plant Assessment was to evaluate rinse tank discharges and plant operating practices. Three areas were examined: a) the levels of metallic concentrations discharging from individual rinse tanks to the sump; b) the levels of cyanide and metals discharging from individual rinse tanks to the cyanide destruction unit; and c) the plant usage of process water.

From Table II (Slide #3) it is readily evident that zinc and iron are the principal metallic contaminants, comprising 55% and 37% respectively, or 92% combined, of the total metal loading of 48 gms/min being treated by the final waste treatment facility. It should also be noted, however, that Tank 51 contains no cyanide and is discharged to the sump while Tank 54 contains significant cyanide levels and is discharged to the cyanide destruc-

Table I
Typical Final Effluent

	Fe	*Zn*	*Cu* (mg/l)	Cr_T	*Ni*	CN_T
Discharge	7.00	3.50	1.00	2.50	2.50	8.00
In-Flow	105.00	157.50	2.40	11.75	7.75	43.20
In/Out Ratio	15.00	45.00	2.40	4.70	3.10	5.40
% Removal	93.30	97.80	58.30	78.70	67.10	81.50

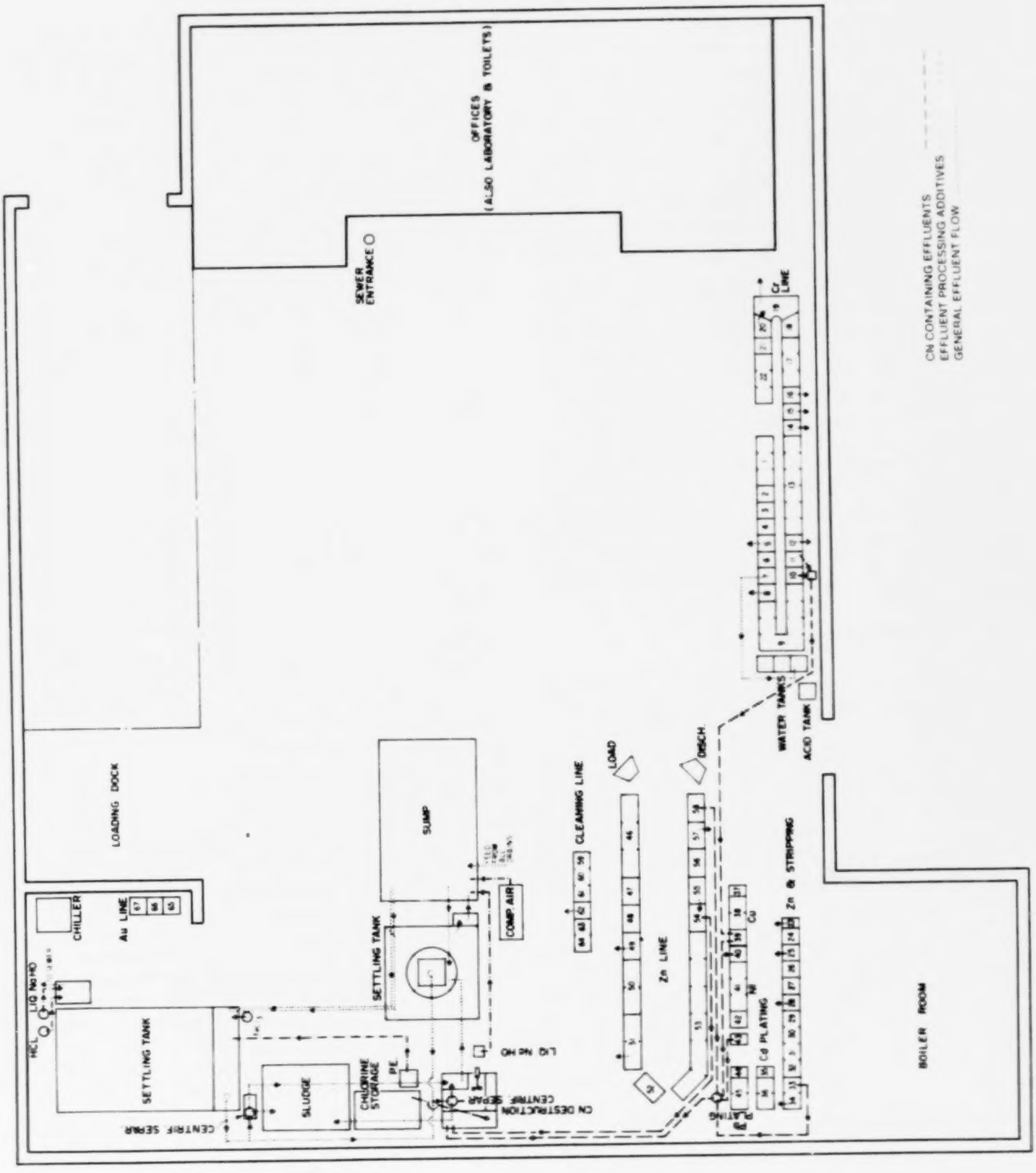
OFFICES (ALSO LABORATORY & TOILETS)
SEWER ENTRANCE
LOADING DOCK
SUMP
CHILLER
Au LINE
LIQ NaHO
HCL
SETTLING TANK
SETTLING TANK
SLUDGE
CHLORINE STORAGE
CENTRIF SEPAR
CN DESTRUCTION CENTRIF SEPAR
LIQ NaHO
COMP AIR
CLEANING LINE
LOAD
DISCH
Zn LINE
Cd PLATING
Ni
Cu
Zn & STRIPPING
PLATING
WATER TANKS
ACID TANK
Cr LINE
BOILER ROOM
CN CONTAINING EFFLUENTS
EFFLUENT PROCESSING ADDITIVES
GENERAL EFFLUENT FLOW

Figure 1 - (Slide No. 1) indicates the physical equipment and piping details as well as the materials and flow balance in an existing plant.

(Figure 1 continued on next page)

TANK	DESCRIPTION	COMPOSITION										PH	WATER OUTFLOW
		Cd	Cr^{T}	Cr^{+6}	Cr^{+3}	Cu	Fe	Ni	Pb	Zn	CN^{-}		
1	CAUSTIC CLEANING BATH												NONE
2	ELECTRIC SOAP CLEANING												NONE
3	ELECTRIC SOAP CLEANING REVERSE POLARITY												NONE
4	RINSE TANK											∽ 13.0	NONE
5	RINSE TANK II		–			<1	–			<1		∽ 10.0	9,5 L/min
6	ACID BATH											∽ 1.5	NONE
7	ACID RINSE		–			0.4	–			0.4		∽ 4.0	10 L/min
8	ACID RINSE II		–			<1	<1	–		<1		∽ 8.0	24 L/min
9	COPPER CYANIDE PLATING BATH											∽ 12.0	NONE
10	COPPER RINSE I		–			528	42	–	–	<1	110	∽ 10.0	2 L/min
11	COPPER RINSE II		–			0.7	–	–		–	1.0	∽ 8.5	4 L/min
12	COPPER RINSE III		–	–		1.2	–	–		–	<1	∽ 1.5	0,5 L/min
13	NICKEL PLATING BATH											∽ 3.3	NONE
14	NICKEL RINSE I		–			<1	<1	352	–	–	<1	∽ 7.0	2 L/min
16	NICKEL RINSE II		–			0.1	–	3.1		–		∽ 8.0	3 L/min
16	NICKEL RINSE III		–			0.1	–	0.3		–		∽ 8.0	2 L/min
17	CHROMIC ACID PLATING BATH											∽ 0.5	NONE
18	CHROMIC ACID DRAG-OUT											∽ 0.7	NONE
19	CHROMIUM RINSE I		180	58	122	209	–	18.7		–		∽ 1.5	1,5 L/min
20	CHROMIUM RINSE II											∽ 6.0	NONE
21	CHROMIUM RINSE III											∽ 7.5	NONE
22	DRIP-DRY AND UNLOADING												NONE
23	RINSE TANK												1,5 L/min
24	CAUSTIC CLEANING BATH (HOT)											∽ 12.5	NONE
25	RINSE TANK		–			0.2	9.1	0.4		2.5		∽ 10.5	2 L/min
26	IDLE NOT IN USE												NOT IN USE
27	HYDROCHLORIC ACID PICKLING BATH											∽ 0.3	NONE
28	RINSE TANK		–			0.1	104	0.6		10.8		VARIABLE	20 L/min
29-32	ZINC PLATING BATH											∽ 12.5	NONE
33	RINSE TANK I												NOT NOW IN USE
34	RINSE TANK II												NOT NOW IN USE
36	CADMIUM PLATING BATH											∽ 12.5	NONE
35	CADMIUM DRAG-OUT											∽ 12.5	NONE
37	RINSE TANK												INTERMITENT SLOW
38	COPPER PLATING BATH											∽ 12.0	NONE
39	COPPER RINSE I		–			183	121	440		0.1	[illegible]	∽ 11.5	SHOULD BE ∽ 6 L/min NOW ∽ 1,5 L/min
40	COPPER RINSE II		–			2.1	0.7	79.2		<1	3.0	∽ 7.5	6 L/min
41	NICKEL PLATING BATH											∽ 4.5	NONE
42	NICKEL RINSE											∽ 7.3	NONE
43	CADMIUM RINSE											∽ 8.2	1,5 L/min
45	LEAD PLATING BATH											∽ 1.4	NONE
44	LEAD DRAG-OUT											∽ 3.5	NONE
46	CAUSTIC CLEANING BATH											∽ 12.7	NONE
47	DRP TANK												NONE
48	ELECTRIC SOAP CLEANING											∽ 12.7	NONE
49	RINSE TANK		–			0.7	3.6	–		3.3		∽ 10.0	8 L/min
50	HYDROCHLORIC ACID PICKLING BATH											∽ 0.5	NONE
51	RINSE TANK		–			0.2	324	–	–	363		∽ 1.5	44 L/min
52	DRIP TANK											∽ 2.3	NONE
53	ZINC CYANIDE PLATING BATH											∽ 12.5	NONE
54	RINSE TANK I		–			0.4	330	–	–	583	470	∽ 12.0	14 L/min
55	RINSE TANK II											∽ 11.0	NONE
56	IRIDATE DIP											∽ 1.6	NONE
57	COLD RINSE TANK		26.4			0.6	9.8	–		275		∽ 5.5	ABOUT 6 L/min
58	HOT RINSE TANK		0.6			1.0	1.0	–		77		∽ 6.0	1 L/min
59-60	CAUSTIC CLEANING TANK											∽ 12.5	NONE
61	RINSE (ACID & CAUSTIC)											VARIABLE	NONE
62-64	ACID CLEANING TANK		9.0			0.7	302	4.5		126		∽ 0.3	TANK 62 – 1,5 L/min TANKS 63 & 64 – NONE
65-67	GOLD PLATING LINE												NONE
	CHILLER												3 L/min

tion unit in the final waste treatment facility. It is also illustrated that the great bulk of the effluent to be treated by the waste treatment facility (26% of the total water and 63% of the total solids) comes from Tank 51. Even with the high flow rate in this rinse tank and the post-rinse drip, iron and acid drag-out into Tank 53, the zinc plating bath, were significant. The significance of proper management of Tank 51 was emphasized to management.

The cyanide level in the final discharge exceeds limits desired and again it was evident from Table II and from the amount of free iron in the final discharge that the majority of this cyanide would be in the form of the stable ferro-cyanide complex. This complex is not amenable to effective treatment by chemical destruction type processes. Therefore, a positive approach to the reduction of this cyanide level by the reduction of free iron available for complexing was recommended to management. This program involved the identification of sources of free iron within each plating line and recommendations to reduce or eliminate these contamination sources.

Process Water Usage

The plant assessment also included a calculation of the process water utilized as compared to management if there are any unforeseen water losses. The water survey in this case was within -8% of the metered amount while not including boiler make-up water and plant domestic usage.

Recommendations were made to management to cut water flows in certain rinse tanks, particularly Tanks 51, 8 and 28 which accounted for approximately 52% of the total plant water usage.

Assessment Survey Results

In all, 13 specific recommendations were made to management. The sequence of implementation was also suggested, and management was requested to report back to H. S. A. as these recommendations were carried out.

To date, a majority of these recommendations have been acted upon and the results are given in Table III (Slide 4).

These results indicate a reduction in zinc contamina-

Table II — Ion flow rates to WTF

Source	*Water* *l/min*	Cr^{+6}	Cr^{+3}	*Cu* *mg/min*	*Fe*	*Ni*	*Zn*	*Cn*	*pH*
Tank 39	1.5	-	-	275.0	182.0	66.0	.15	582.0	11.5
43	1.5								8.2
54	14.0	-	-	22.0	700.0	-	8150.00	6580.0	12.6
58	1.0	.6	-	1.0	1.0	-	77.0	-	6.5
33									
total to Cn destruct	18	.6	-	298.0	883.-	66.0	8227.15	7162.-	
Tank 5	9.5	-	-	0.1	-	-	0.1	-	10.0
7	10.0	-	-	4.0	2.4	-	2.4	-	8.0
8	24.0	-	-	2.4	2.4	-	2.4	-	8.0
10 (partial only)	0.5	-	-	26.4	21.0	-	-	50.0	10.0
11	4.0	-	-	2.8	-	-	-	4.0	8.5
12	0.5	-	-	0.6	-	-	-	-	1.5
14	2.0	-	-	0.2	0.2	704.0	-	- 7.0	
15	3.0	-	-	0.3	-	9.3	-	-	7.5
16	2.0	-	-	0.2	-	0.6	-	-	7.0
19	1.5	88.0	1682.0	31.4	-	28.0	-	-	1.5
23	1.5	-	-	-	-	-	-	-	-
25	2.0	-	-	0.4	18.2	0.8	5.0	-	10.5
28	20.0	-	-	2.0	2080.0	12.0	216.0	-	variable
40	6.0	-	-	13.0	4.2	475.0	0.6	18.0	7.5
49	8.0	-	-	5.6	28.8	-	26.4	-	10.0
51	44.0	-	-	13.2	14256.0	-	15972.-	-	1.5
57	6.0	158.0	-	3.6	58.6	-	1650.0	-	5.5
62	1.5	13.5	-	1.0	453.0	6.7	189.0	-	variable
Chiller	3.0	-	-	-	-	-	-	-	
Total to sump	149.0	259.5	1682.0	107.2	16922.4	1236.4	18065.50	72.0	
Total	167.0	260.1	1682.0	405.2	17805.4	1302.4	26292.65		
Total metals	47,747.8 mg min or 47.7 gm min								
% of Total metals			0.54	3.52	0.85	37.29	2.73	55.07	

Table III
Changes in Final Effluent Characteristics
Metallic and Cyanide Contamination Levels

ion/mg/L	*Cu*	*Ni*	*Cd*	*Zn*	CN_T
Before	1.0	2.5	0.1	3.5	8.0
After*	1.1	2.6	0.1	2.2	2.2

*based on average of 5 analysis

Plant Water Usage

Before	57,000 gpd - months April, May, June
After	39,000 gpd - months September, October

tion of 37%, of cyanides by 72% and a reduction in process water utilized of 32%.

The results indicate what can be done by management simply by critically examining their own facilities and plant practice. It is also evident, however, that the contamination levels achieved, while significantly lower, are still not low enough to meet legislated or proposed effluent guideline limits.

The important factor is that management has now reviewed the existing conditions and optimized them. It is now ready to examine various alternatives in pollution control technology.

One of the areas of control technology previously mentioned is that of electrolytic technology and of specific interest is the field of electrochemical treatment methods.

In conjunction with the above plant assessment, H. S. A. operated an industrial scale electrochemical research reactor system in the same plant.

THE H.S.A. REACTOR SYSTEM

Electrochemical Technology

In recent years, there has been increased activity in the electrochemical reactor field as the significance and potential advantages of electrochemical process are being more widely realized. Electrochemical treatment of pollution is an attractive idea, by virtue of its unique "clean" system where oxidation and reduction take place via an inert electron, without the need of chemical additions.

Electrochemical treatment of effluents has been postulated for some time, however, owing to unsatisfactory reactor design, it could not be used to handle large volumes efficiently and at a low cost. The recent development of a carbon fibre-based reactor by H. S. A. Reactors Limited[1,2] has made it possible to achieve real time effluent treatment, at low cost.

Some of the possible applications of the electrochemical effluent treatment include the reduction process, such as the removal of heavy metals, including copper, nickel, lead, zinc, cadmium, gold and silver, and the subsequent recovery of the metals.[3-7] Reduction of the hexavalent chromium from plating liquors is another example. Further examples in the oxidation process are the decomposition of cyanides, phenols, acetates and other organic compounds. A review of electrochemical treatment of effluents is given by Kuhn and others.[6,7]

Carbon Fibre Reactor Design

The patented carbon fibre reactor being developed by H. S. A.[1,2] radically changes the "potential" of the electrochemical systems for effluent treatment. Most electrochemical processes are limited by mass transfer rates and attempts have been made to develop reactors with greater mass transfer capabilities, for example the fluidized bed, the packed bed, and other three-dimensional particulate reactors.[4, 8] The limitations of these are well documented[9, 10], and include non-uniformity of potential distribution.

The primary design characteristic of the carbon fibre is the increase of mass transfer rates while simultaneously having a controllable and uniform electrode potential over the entire electrode surface. The carbon fibres are commercially produced by the high temperature pyrolysis of precursor materials such as poly-acrylonitrile, and have very favourable properties as electrode material because of its hard vitreous surfaces, electrical conductivity and high hydrogen and oxygen over-voltage characteristics. Additionally, the fibres have high modulus, low density, good thermal conductivity, very low coefficient of thermal expansion, chemical inertness, thermal shock resistance, a high vibration damping factor and excellent fatigue resistance.

Another important property of carbon fibres is its enormous surface area. The fibres are typically between 5 to 15 microns[11] in diameter, and one gram of fibre has a surface area of 2.6×10^6 cm.[2] This surface area is about 1,000 times larger than the surface area per unit volume of other types of particulate reactors. As a result of this increased surface area, the mass transfer rates in this reactor approach those achieved by some heterogeneous catalytic reactors. The major operational advantages of the reactor are: 1. It can operate at lower current densities without a corresponding decrease in output. This results in a sharp decrease in the cost per unit of effluent treated.; 2. It is possible to operate processes at a high throughput in a realistic time-scale (in the order of seconds).; 3. A reduction in the capital cost is achieved because effluent can usually be treated in a single pass process through appropriate design considerations.

Electrochemical Effluent Treatment - Pilot Test

Introduction

Research at the laboratory bench scale led to the development of a process utilizing the carbon-fibre electrochemical reactor, by which cyanides, metal cyanides and heavy metal could be removed from effluents generated by the metal finishing industry.

It has been found that the process can electro-oxidize and destroy cyanides and metal cyanide complexes more effectively than the alkali-chlorination process and at only a fraction of the cost. Free cyanides and cyanide complexes of zinc, copper and cadmium could be completely destroyed, such that after treatment, cyanide could not be detected in the effluent. The heavy metals, including metal complexes of various chelating agents, could be electro-reduced, and the metals recovered in the cathode.

As a result of the unique electrochemical properties of the carbon fibres, including large hydrogen and oxygen over-potentials, controllable and uniform current and potential distribution, chemical inertness and high mass transfer, it was possible to effect complete removal of pollutants in residence times in the order of seconds.

During the summer of 1977 an industrial-scale, electrochemical research system was constructed by H. S. A. in Toronto and shipped by truck to a metal finishing plant for pilot plant testing. The design of the system permitted it to be commissioned the day of delivery. The system operated for five weeks on both the final effluent from the plant and all rinse tank discharges.

Operation on Final Plant Discharge

The objective of the pilot test-work was to operate the system in real plant conditions, to examine the system's ability to efficiently and effectively destroy cyanide, the cyanide-metal complexes (including the stable ferrocyanide complex), while simultaneously removing the contained trace metallics.

The success of the testwork was to reduce the total metallic concentration in the final effluent to less than 1 mg/L (ppm) and reduce the total cyanide to an undetectable level (analytically given as 0.1 mg/l).

Table IV (Slide 5) illustrates the input/output of the final plant effluent through the H. S. A. reactor system.

Operation on Rinse Tank Discharge

Since the majority of the environmental objectionable species in the metal finishing industry wastewaters come from the discharge of rinse tanks, the reactor system was applied to the discharges from zinc, copper, cadmium, chromium, nickel and lead rinse tanks.

Table IV
Final Plant Effluent Characteristics
Before and After Electrochemical Treatment

Species	*Before Electrochemical Treatment (mg/L) (Currently discharged to sewer)*	*After Electrochemical Treatment (mg/L)*
Cyanide$_T$	7.5	< 0.1
Lead	0.1	< 0.1
Zinc	2.7	0.3
Cadmium	0.3	< 0.1
Chromium$_T$	2.1	0.1
Nickel	2.3	0.1
Copper	0.4	< 0.1

Reactor voltage of 19.4 Volts at 63 Amps.

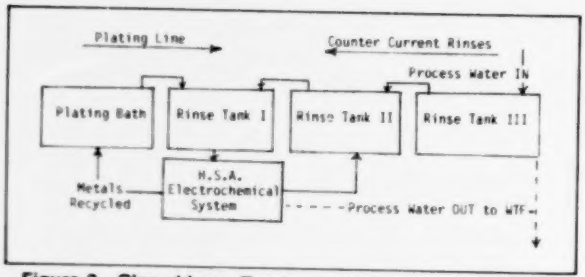

Figure 2 - Closed Loop Treatment of rinse tank discharge.

If the rinse tank discharges are treated at their point of origin, such that there is only a limited rinse tank discharge, then the size of the general wastewater treatment system for the final effluent from the plant can be smaller and less costly. Figure 2 (Slide No. 6) schematically illustrates such rinse tank process control.

The advantages of treating the rinse tank discharge are: 1. the possibility of significantly reducing the discharge of wastewater; 2. the economic recovery of drag-out metals which can then be recycled to the plating bath; 3. the installation of recycling units, obviating the necessity of constructing a large general wastewater treatment facility.

The H. S. A. electrochemical system was tested for its applicability in the following rinse tanks in a metal finishing plant: a) Cadmium Rinse; b) Copper Rinse; c) Nickel Rinse; d) Chromate Rinse; e)Zinc Rinse; f) Lead Rinse.

Laboratory bench scale tests were carried out on other possible rinses such as electroless nickel.

Treatment of Cadmium Rinse Tank Discharge

The input/output results of the cadmium rinse are given in Table V.

As the rinse tank discharge is recycled, according to Figure 2, the output from the electrochemical treatment system does not have to meet the stringent clean up regulations.

Treatment of Copper Rinse Tank Discharge

The input/output results of treating the copper rinse discharge are shown in Table VI.

Figure 3 graphically shows the copper removal and cyanide reduction achieved electrochemically.

Treatment of Nickel Rinse Tank Discharge

The input/output of the electrochemical system for the nickel rinse is shown in Table VII. The nickel plating was carried out on an acid bath.

Treatment of Chromate Rinse Tank Discharge

The input/output of the electrochemical system for the chromate rinse is shown in Table VIII.

Treatment of Zinc Rinse Tank Effluent

The zinc plating was being carried out in a cyanide bath

TABLE V

Cadmium Rinse Tank Effluent (pH = 11.7, σ = 7820) at a Reactor Voltage of 11-12 V at 375-510 A

Before Electrochemical Treatment	*(mg/L)*	*After Electrochemical Treatment (mg/L)*	*Percent Removal*
Cadmium	158	3.1	98
Cyanide	2180	72.5	97

TABLE VI

Copper Rinse Tank Effluent (pH = 10.6,σ = 2700) at a Reactor Voltage of 12 V at 370 A

	Effluent Before Electrochemical Treatment (mg/L)	*Effluent After Electrochemical Treatment (mg/L)*
Copper	121	0.70
Cyanide (total)	270	3.35

TABLE VII

Nickel Rinse Tank Effluent (pH = 7.8, σ = 9650)

	Before Electrochemical Treatment (mg/L)	*After Electrochemical Treatment (mg/L)*
Nickel	132.0	14.5

TABLE VIII

Chromate Rinse Tank Effluent

Before Electrochemical Treatment (mg/L)	*After Electrochemical Treatment (mg/L)*
2,310	71.5

TABLE IX

Zinc Rinse

Before Electrochemical Treatment	*(mg/L)*	*After Electrochemical Treatment (mg/L)*
Zinc	352.0	0.7
Cyanide	258.0	12.0

TABLE X

Lead Rinse

Before Electrochemical Treatment (mg/L)	*After Electrochemical Treatment (mg/L)*
1,180	26.4

The conductivity of the rinse tank was 2,420 μ mho cm^{-1}.

TABLE XI

Electro-oxidation of Cyanide and Metal Cyanides

Before Electrochemical Treatment	*(mg/L)*	*After Electrochemical Treatment (mg/L)*
Zinc	117	0.27
Copper	842	0.50
Cyanide	1,230	< 0.10

and Table IX gives the input/output analysis in the electrochemical system. The conductivity of this rinse tank varied between 6,200 to 9,500 umho cm^{-1}.

Treatment of Lead Rinse Tank Effluent

The lead plating was being carried out in an acid bath. Table X shows the input/output of the electrochemical system for the lead rinse.

The conductivity of the rinse tank was 2,420 umho cm^{-1}.

Cyanide Destruction

The electrochemical system can effectively destroy cyanide, metal cyanide complexes, and remove the metals without involving the problems of sludge handling, dewatering and disposal. This is illustrated in Table XI. The electrochemical system is estimated to operate at approximately one-sixth the cost of an alkali-chlorination unit.

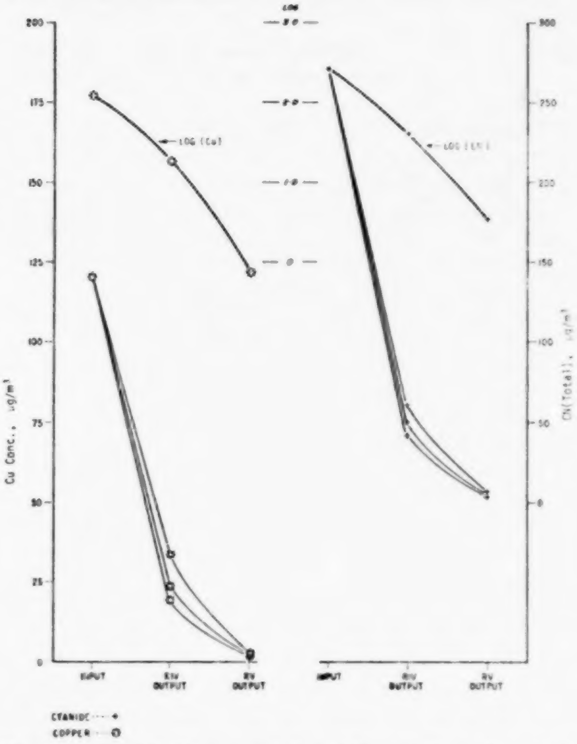

Figure 3 - Graphical Representation of Copper-Rinse Treatment by Two Reactors in Series.

Conclusions

In general the results of the test programme are excellent in that the reactor system achieved a significant reduction of cyanide and metallic contamination in the final effluent. This reduction is greater than 99% in most cases. The application of the H. S. A. system to the final effluent should meet any proposed legislative standards for the metal finishing industry.

The electrochemical reactors installed were designed only for the treatment of final effluent. This effluent is currently discharged directly to the municipal sewers.

This reactor system, although not designed for the treatment of rinse tank discharges, was nevertheless successfully utilized in this application. The results obtained, as given in Table V to XI, indicate the reduction of the toxic metals to a level where the rinse tank waters could form a closed loop resulting in a significant reduction in process water usage with the objective of attaining *a zero discharge* state.

The H. S. A. reactor system effectively operated on final waste streams and on rinse tank discharges. The reactor destroyed cyanides, metal cyanide complexes and removed trace metallics in both discharges. The reactor system does not produce sludge. The treated stream, particularly the rinse tank stream, could be recycled as plant process water resulting in considerable conservation of plant water usage. The system is expected to be cost competitive in both capital and operating cost areas.

Additionally, the results have also indicated that the H. S. A. reactor system will:

- be of value to all sizes of metal finishing and plating plants, particularly small plants, in achieving low limits;
- because the system is physically small in size and modular in design, accommodate changes in plant output (discharge) by the addition or removal of reactor units. Thus the plant expansion or increased productive capacity can easily be accommodated by reactor unit additions to the initial installation with a minimum of disruption to the plant;
- operate on final effluent discharges before or after a Waste Treatment Facility (WTF) or directly on pollution source - the rinse tanks; in all applications be it the rinse tank or final effluent, the reactor system is an online system with the residence time in the reactor in the order of seconds;
- resolve many of the current problems concerned with sludge since NO SLUDGE IS PRODUCED but rather sheets of metal or concentrated metal liquors in a chemically suitable form for recycling to plating baths;
- promote the re-use of process rinse waters by the continuous, on-line removal of contaminants;
- permit the freeing of floor space for added production facilities because of the small size of the reactor units compared to bulky and inefficient conventional WTF's;
- be more than economically competitive on a capital basis with conventional WTF's and operate at a fraction of the cost. For example, from the results of the research test plant it is estimated that for a plant with a final discharge from WTF of 30 gpm that an H. S. A. system for this application would have a capital cost of approximately $50,000 U. S. and operating cost of approximately 80¢ per hour at 2¢ per kilowatt hour, or approximately 0.044¢ per gallon treated.

The H. S. A. electrochemical pollution control system is not yet commercially available, although production is expected to commence early in 1978 for specific applications such as electroless nickel, and latter 1978 for all other applications. H. S. A. plans to demonstrate a full plant system in Cincinnati in mid 1978 under the auspices of a Joint Demonstration Project sponsored by the E.P.A. and the Metal Finishers' Foundation. This Joint Demonstration Program sponsored by the NAMF and EPA plans to demonstrate the technical and economic viability of the treatment of effluent from the metal finishing industry utilizing the electrochemical waste treatment system. The plant demonstration in three phases is estimated to take approximately 15 months as follows:

Phase I - 5 months for plant assesment, final design, construction and installation of the reactor system

Phase II - 6 months of continuous operation in the plant of the designated system

Phase III - 4 months for analysis and evaluation of the operation and preparation of a final report of the program.

We are, however, currently engaged in providing Plant Assessment Services to the Metal Finishing Industry.

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Sulfide - vs - Hydroxide Precipitation of Heavy Metals From Industrial Wastewater

A. K. Robinson*

INTRODUCTION

The most widely used method of removing heavy metals from wastewater today is the hydroxide process. Lime is used to raise the pH of the water, and the heavy metals are concentrated into a sludge which is usually trucked away to landfill. The hydroxide process removes heavy metals in general down to 1 or 2 mg/l.

With increasing emphasis on protection of our environment, new methods of removing heavy metals from water are being sought. One of these is the sulfide process which offers considerable promise on account of the far lower solubilities of heavy metal sulfides compared with the corresponding hydroxides.

This paper reviews the two processes, hydroxide and sulfide, indicates some of the advantages and disadvantages of each, and outlines our planned work in this area.

Wastewaters Treated

The metal finishing and metal producing industries produce an extremely wide range of wastewaters containing heavy metals from rinse waters containing a few mg/l, to concentrated dumped process solutions containing several hundred thousand mg/l. The principal heavy metals of concern in these wastewaters are arsenic, cadmium, chromium, copper, lead, manganese, mercury, nickel, selenium, and zinc.

Concentrated waste process solutions are often treated in practice along with dilute wastewater streams, by "bleeding" them over a period of time into the dilute stream.

THE HYDROXIDE PROCESS

Clarifier Operation

Precipitation of the hydroxide takes place when the pH of the wastewater is raised from its normally acid condition to pH 8-11. Except in small operations, the process is continuous rather than batch, and large circular tanks known as "clarifiers", are common. Figure 1 shows such a clarifier. Freshly-slaked "hot pebble lime" (quicklime, CaO) is generally used, on account of its low cost and ease of handling, to raise the pH, although in some cases sodium hydroxide may be used. Polyelectrolytes are usually added, in amounts from 0.1 to 1.0 mg/l, at the same time as the lime addition. They can dramatically improve the settling characteristics of the hydroxide precipitate (References 2, 6).

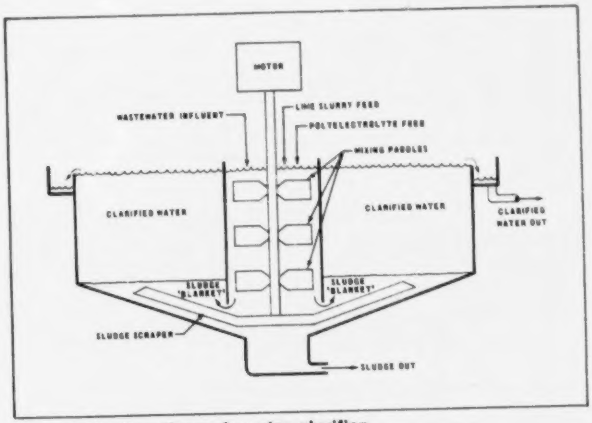

Fig. 1—Section through water clarifier.

Cr (II)	Cr (III)	Cr (VI)
Cr^{2+} exists in solution	Cr^{3+} exists in solution	Cr^{6+} does not exist in solution
$Cr(OH)_2$ chromous hydroxide exists only in strong reducing conditions	$Cr(OH)_3 \cdot 3H_2O$ green chromic hydroxide precipitated in alkaline solutions	$Cr(OH)_6$ does not exist
chromous salts eg. $CrSO_4$	chromic salts eg. $Cr_2(SO_4)_3$	chromates $(CrO_4)^{2-}$ dichromates $(Cr_2O_7)^{2-}$

Fig. 2—Chromium compounds.

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Pretreatments Before Clarification

Chrome Reduction

The metal chromium may be present in a wastewater as trivalent chromium (chromic salts) or as hexavalent chromium where it forms part of the anion (Figure 2).

If hexavalent chromium is present - and it usually is - then it must be reduced to the trivalent form before feeding to the clarifier. Unless this is done, the hexavalent chromium will pass through the clarifier unchanged. Hexavalent chrome reduction is commonly accomplished by reducing pH to approximately 2 and adding ing sulfur dioxide or sodium bisulfite (Reference 2). Control of the reduction is readily automated, using ORP (oxidation-reduction-potential) electrodes. Sufficient retention-tank capacity must be provided to allow time for the reaction to proceed to completion (approx. 45 minutes, depending on pH) (Figure 3).

Cyanide Removal

Where cyanide-containing streams are present, these are pre-treated separately to destroy cyanide, before entering the main wastewater stream for removal of heavy metals. Batch operation of an alkaline chlorination process is often employed (References 2, 6).

Sludge

Sludge from the clarifier will contain up to 3% solids, depending on the settling time allowed. Further dewatering, to reduce the cost of trucking the sludge away, is accomplished by natural evaporation in a lagoon, or by centrifuging, or by filtration. The dewatered sludge contains 12 - 18% solids.

Overall Hydroxide Process

Figure 4 is an aerial view of a hydroxide plant treating 1.5 Ml/day (400,000 gal/day) wastewater from an airplane factory.

The heavy metal reductions achieved by this plant are given in Figure 5 (Reference 5). The lime dosage is approximately 200 mg/l. These overall reductions are somewhat better than claimed in the literature (Reference 3).

Figure 6 summarizes the reported levels of heavy metals in effluents treated by the hydroxide process.

Effect of Complexing and Chelating Agents

No description of the removal of heavy metals from wastewater would be complete without a reference to complexing and chelating agents. These materials are universally added to metal finishing solutions for a wide variety of purposes, including brightening, cleaning, and solubilizing of metals. These agents are known to inhibit and even prevent the precipitation of heavy metals. Some of the commonly used ones are: tartrates, phosphates, ethylenediaminetetra-acetic acid (EDTA), and ammonia. Unfortunately, exact knowledge of the effect of complexing and chelating agents on hydroxide precipitation is not available, largely because of their proprietary nature.

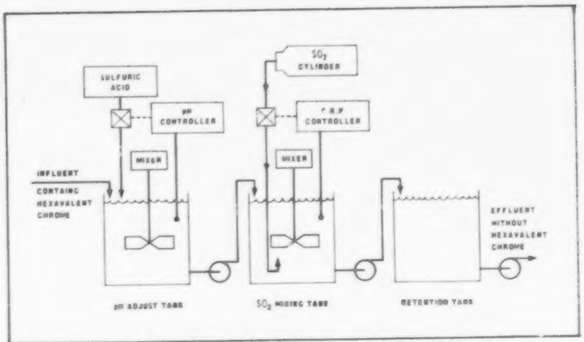

Fig. 3—Process for reduction of hexavalent chromium.

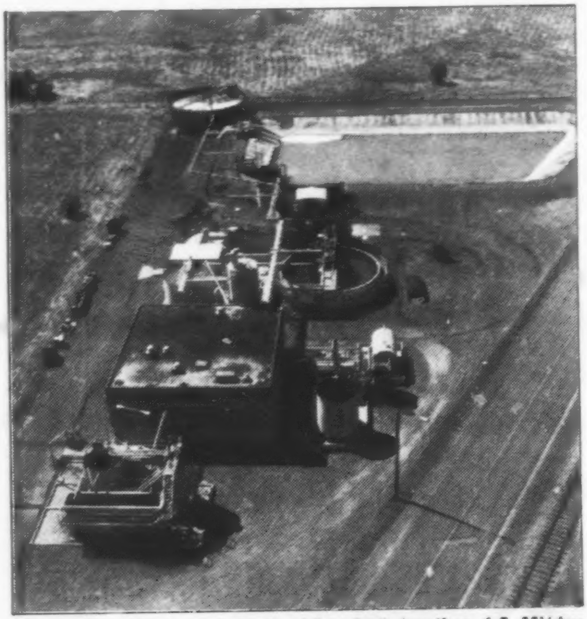

Fig. 4—Aerial view of hydroxide plant treating 1.5 Ml/day (400,000 gal/day) wastewater from an airplane factory.

INFLUENT mg/l		EFFLUENT Daily Maximum Allowed by State Permit mg/l
Cu	1 - 10	0.10
Cd	0 - 2	0.03
Ni	0 - 1	0.10
Zn	0 - 2	0.10
Cr (hexavalent)	2 - 20	
Cr (total)	6 - 60	0.25

Fig. 5—Influent and effluent heavy metal concentrations for hydroxide plant of Figure 4.

Heavy Metal	mg/l Concentration
Cu	0.0 - 2.5
Cd	0.0 - 1.0
Ni	0.09 - 1.9
Zn	0.02 - 5.4
Cr (trivalent)	0.06 - 0.75
Cr (total)	0.06 - 4.6

Fig. 6—Hydroxide process - reported levels of heavy metals after treatment.

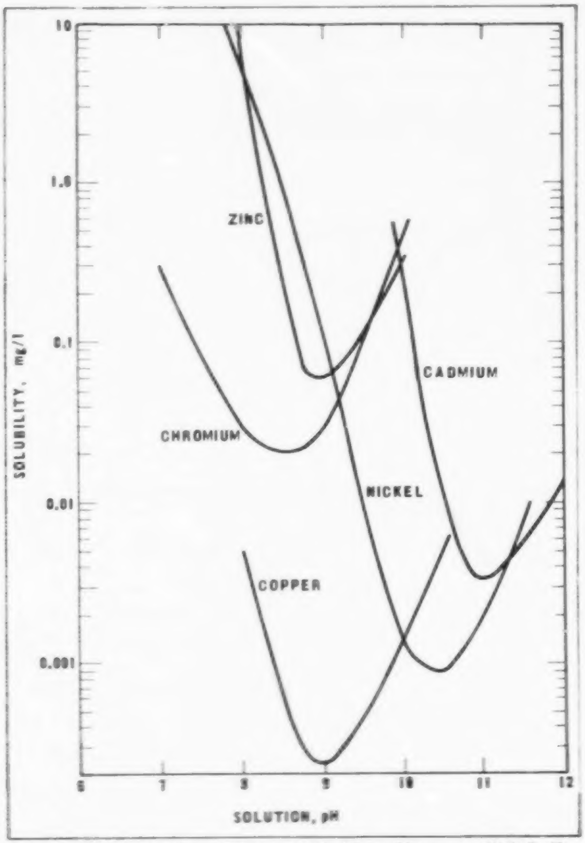

Fig. 7—Effect of pH on the concentration of heavy metals in the effluent.

Effect of pH on Precipitation

Reference to Figure 7 shows that the optimum pH for precipitation is different for different metals. Consequently, any treatment plant receiving a mixed heavy metal load must adopt a compromise pH value. A pH of 8.5 or 9.0 is often employed. If a higher pH must be used, eg. pH 11 for cadmium removal, then subsequent acidification of the effluent will be required if the local discharge permit requires a pH maximum of 9, as many do (Reference 7).

THE SULFIDE PROCESS

Advantages of the Sulfide Process

Comparative Solubilities of Sulfides and Hydroxides

The chief attraction of the sulfide process lies in the extremely low solubilities of most metal sulfides. Figure 8 lists the calculated solubilities of some heavy metal sulfides compared with the corresponding solubilities of their hydroxides. In this list, the solubilities of the sulfides are calculated at a pH of 8.0, and those of the hydroxides at the optimum pH within the range 7-11 (References 8, 9, 10 and 16).

METAL	SOLUBILITY		
	Hydroxide (minimum) Solubility, mg/l	pH	Sulfide Solubility at pH 8.0 mg/l
Iron	1.8×10^{-3}	10.5	3.0×10^{-6}
Nickel	9.0×10^{-4}	10.5	1.6×10^{-7}
Zinc	6.0×10^{-2}	9.0	1.4×10^{-10}
Cadmium	3.6×10^{-3}	11.0	7.6×10^{-15}
Tin			1.0×10^{-13}
Lead	4.1×10^{0}	9.3	1.4×10^{-15}
Copper	2.5×10^{-4}	9.0	3.4×10^{-24}
Mercury			2.7×10^{-40}
Silver			7.9×10^{-17}
Chromium	2.0×10^{-2}	8.5	

Fig. 8—Theoretical solubilities of sulfides and hydroxides.

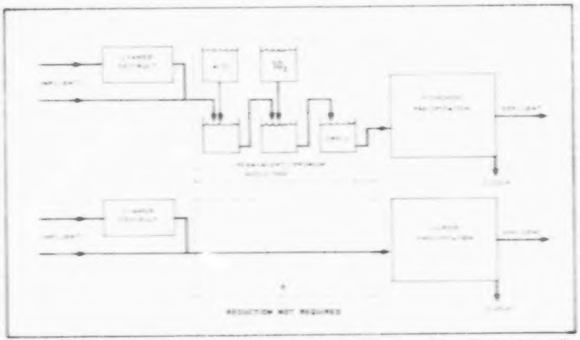

Fig. 9—Elimination of hexavalent chrome reduction step by sulfide precipitation process.

Removal of Hexavalent Chromium by Sulfides

A second attraction of the sulfide process is its ability to remove chromates and dichromates, i. e. - hexavalent chromium, from wastewater, without preliminary reduction of the chromium to its trivalent state. As shown in Figure 9, this eliminates, in a conventional sulfur dioxide reduction plant, two tanks, with their associated pH and ORP controls, and the sulfuric acid, sulfur dioxide, and lime needed to lower pH, reduce, and restore pH during the pretreatment.

Removal of Complexed Heavy Metals

A third advantage of the sulfide process is its increased ability to precipitate metals complexed with at least some complexing agents. Figure 10 shows the effluents, in a laboratory test, from an input containing heavy metals complexed with tartrates (Reference 1).

Disadvantages of the Sulfide Process

General

Up to this point, the sulfide process has been referred to as if it were a single, well-defined process. In fact, there are at least four main varieties of sulfide process, and although the advantages claimed apply to all four, the disadvantages listed here do not necessarily apply to all varieties of the process.

Odor and Toxicity of Hydrogen Sulfide

This gas is released if dilute acids contact sulfides. According to Reference 3, air containing:

0.075 mg/m^3 may darken paints
0.5 mg/m^3 has a distinct odor
30 - 50 mg/m^3 has a strong odor
1400 mg/m^3 is fatal in 30 minutes

Under normal alkaline operating conditions risk of H_2S evolution is minimal. However, adequate safety precautions would have to be taken in any plant employing a sulfide process in conjunction with possibly acid wastes, to ensure that accidental mixing of sulfide and acid could not occur.

Cost of Precipitant

Figure 11 shows a direct comparison of the cost of precipitating, using lime for the hydroxide and sodium sulfide or hydrosulfide for the source of sulfide (Reference 4). The "Sulfex" process uses ferrous sulfide as the precipitant, and some additional chemical cost results from the cost of the iron used in the preparation of this precipitant.

Use of Sulfide as a "Polishing" Operation After Lime Precipitation

The higher chemical cost of the sulfide process - at least 14 times that of the lime process, as can be seen in Figure 11 - suggests the possibility of a two-stage operation. Lime precipitation could be used to remove the greater part of the heavy metal load, and the sulfide operation could follow, to remove heavy metals to a level unattainable by lime alone.

The additional cost and complication of a sulfide "polishing" stage would be offset by elimination of the chrome reduction stage before the lime precipitation.

It should be pointed out that very little is known of the effectiveness of sulfide precipitation in extremely dilute (below 2 ppm) solutions. If a "sludge blanket" technique were found to be essential to the success of the process, then several days' operation might be necessary to build-up sufficient sludge for effective blanketing.

Metal	Influent concentration, mg/l	Effluent Concentration, mg/l	
		Hydroxide Process	Sulfide* Process
COPPER	4	1.5	0.01
CADMIUM	4	1.7	$<$ 0.01
CHROMIUM (TRIVALENT)	4	2.0	3.50
NICKEL	4	3.0	$\leqslant$ 0.40
ZINC	4	1.0	$\leqslant$ 0.03

*"Sulfex" Process

Fig. 10—Comparison of sulfide and hydroxide process residuals for an influent containing Rochelle salt complexing agent.

Chemical	Price per ton	Price per 100 lb of metal precipitated*
Lime, CaO	$28.75	$1.27
Sodium Sulfide Flake, 60% Na_2S	$275	$28.15
Sodium Hydrosulfide Flake, 71% NaHS	$305	$18.93

*Calculated for copper.

Fig. 11—Raw chemical cost comparison, lime - vs - sulfides. (October 1977).

Type	Precipitant	Co-Precipitant
A	Soluble Sulfide	None
B	Soluble Sulfide	Hydroxide
C	"Insoluble" sulfide	None
D	"Insoluble" Sulfide	Hydroxide

Fig. 12—The four principal types of sulfide precipitation.

Disposal of Sulfide Sludge

Disposal of metallic sulfide sludges may pose a considerable problem, compared with disposal of the corresponding hydroxide sludges which have an established history of disposal as landfill. At least three suspicions

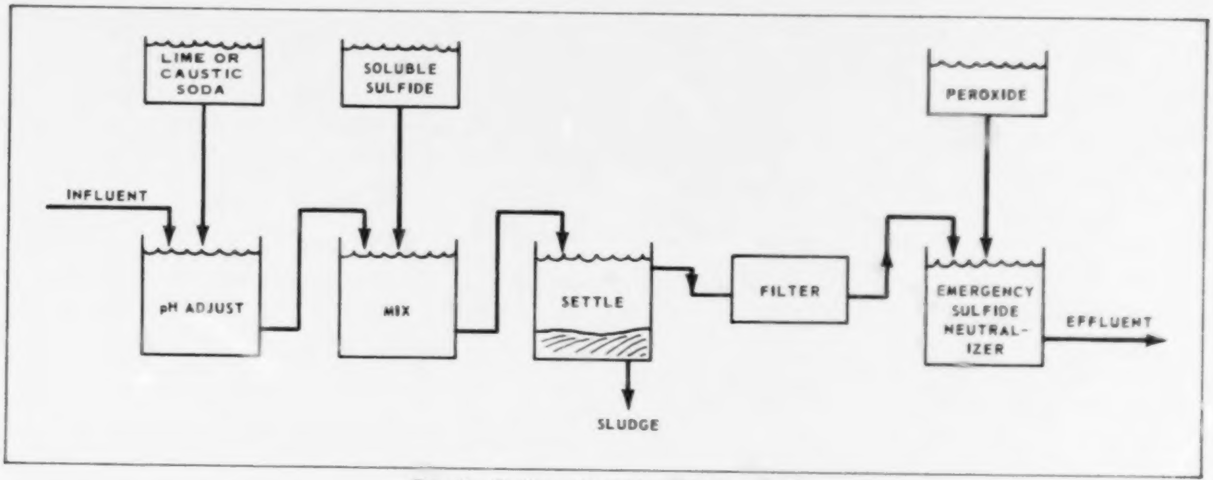
LIME OR CAUSTIC SODA
SOLUBLE SULFIDE
PEROXIDE
INFLUENT
pH ADJUST
MIX
SETTLE
FILTER
EMERGENCY SULFIDE NEUTRALIZER
EFFLUENT
SLUDGE

Fig. 13—Outline of soluble sulfide process.

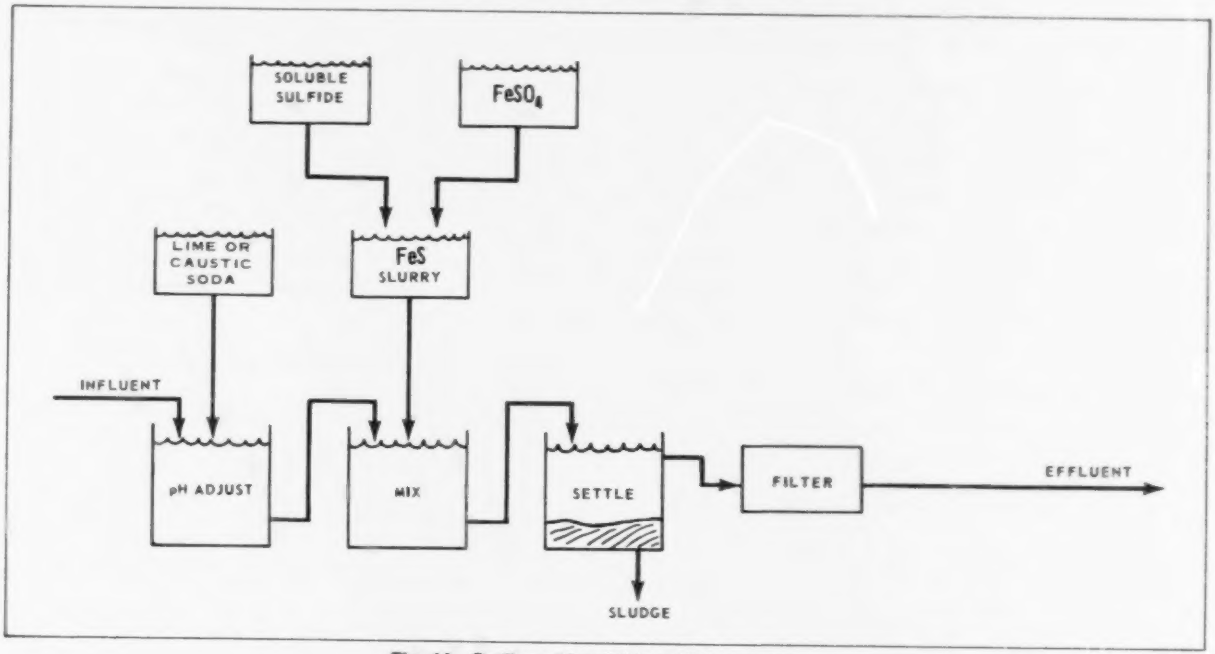
SOLUBLE SULFIDE
$FeSO_4$
LIME OR CAUSTIC SODA
FeS SLURRY
INFLUENT
pH ADJUST
MIX
SETTLE
FILTER
EFFLUENT
SLUDGE

Fig. 14—Outline of insoluble sulfide process.

will have to be overcome before sulfide sludges could become accepted as conventional landfill: (a) The suspicion that hydrogen sulfide might be released to the atmosphere, creating at least a nuisance, and possibly a toxic hazard, (b) Toxic metals might be leached out and find their way into surface waters, (c) The sulfide might oxidize to sulfate and release dilute sulfuric acid to surface waters (this is a problem with certain mine tailings).

Description of the Sulfide Processes

Soluble and Insoluble Sulfides

At the present time, both soluble and insoluble sulfides (References 11 and 12) are used, and each may be reacted in the presence of lime as a co-precipitant, so that four main processes are employed, as in Figure 12.

Soluble Sulfide Processes

Figure 13 outlines a process using soluble sulfide, such as sodium sulfide or sodium hydrosulfide. Hydrogen sulfide is available in liquid form and could also conceivably be used.

A "specific ion" sulfide-sensitive electrode is used in a manner analogous to a pH probe, to control the addition of soluble sulfide (Reference 15). Metallic sulfide precipitates may be partly colloidal and show poor settling characteristics unless special precautions are taken. Use of a "sludge blanket" technique in which the precipitating solution is allowed to pass through a blanket of previously-formed sludge solution is a well known method (Reference 6). The particles in the previously-formed sludge grow larger in the blanket, and formation of smaller individual colloid-sized particles is minimized. Lime is used with or without the sludge blanket to form a gelatinous hydroxide precipitate to capture colloidal particles. Polyelectrolyte aids are also used.

Insoluble Sulfide Processes

Figure 14 shows a process using "insoluble" ferrous sulfide. In fact, "insoluble" is a relative term, and even ferrous sulfide, with a solubility product as low as 3.7×10^{-19}, still provides enough soluble sulfide for sulfide precipitation to occur. The only requirements are: a. that the metal to be precipitated must have an even lower solubility than ferrous sulfide (Reference 12), and b. sufficient solid ferrous sulfide to be present to replace the sulfide ions withdrawn from solution by the precipitated metal.

Figure 15 lists sulfides and their solubility products. Iron sulfide will precipitate all sulfides below it in the table. As with the soluble sulfide process, lime and a polyelectrolyte may be used, and a sludge blanket is an effective way of avoiding the problem of colloid formation.

Position of Sulfide Precipitation Today

In contrast to the hydroxide precipitation method, there is no extensive history of industrial use at present: only a small number of plants are in construction or initial operation.

BOEING WORK ON THE SULFIDE PROCESS

The Manufacturing Research and Development organization of The Boeing Commercial Airplane Company has a cost-sharing grant agreement (Reference 13) with the EPA to build a laboratory-scale plant for treating industrial wastewaters by the sulfide and hydroxide processes (Reference 13). Samples of wastewater will be collected from typical metal finishers across the United States, and comparisons will be made between the two processes. Quality of effluent will be measured by atomic absorption equipment capable of analyzing for heavy metals in the p.p.b. range. Optimum operating conditions will be selected for both sulfide and hydroxide processes, in what is planned to be an objective, impartial study. The study will include cost analysis.

Metal Sulfide	Solubility Product Ksp
MnS	1.4×10^{-15}
FeS	3.7×10^{-19}
ZnS	1.2×10^{-23}
NiS	1.4×19^{-24}
SnS	1.0×10^{-25}
CoS	3.0×10^{-26}
PbS	3.4×10^{-28}
CdS	3.6×10^{-29}
Ag_2S	1.6×10^{-49}
Bi_2S_3	1.0×10^{-97}
CuS	8.5×10^{-45}
HgS	2.0×10^{-49}

Fig. 15—List of metal sulfide solubility products.

SUMMARY AND CONCLUSIONS

More complete removal of heavy metals from wastewater is claimed for sulfide precipitation than is possible by the well-established hydroxide process. In general the hydroxide process reduces metals — unless complexing agents are present — to the 0.1 to 2 mg/l level, and it is claimed that the sulfide process reduces metals to the 0.05 mg/l level, or better.

The sulfide process has the additional advantage of not requiring preliminary reduction of hexavalent chromium to trivalent chromium. However, the sulfide process does have the disadvantages of higher cost (unless offset by elimination of hexavalent chromium reduction), odor, toxicity, greater sophistication, and possibly, sludge disposal problems.

Additional work is currently in progress that will lead to more precise definition of the advantages of the sulfide process.

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Evaluation of Advanced Reverse Osmosis Membranes For the Treatment of Electroplating Wastes

Kenneth J. McNulty, Peter R. Hoover & Robert L. Goldsmith*

ABSTRACT

Because of the limited pH range over which current commercially available reverse osmosis membranes can be applied, a test program was initiated to define the applicability of new membrane materials to the treatment of rinsewaters with extreme pH levels and high oxidant levels (chromic acid). Life tests were conducted with the PA-300, PBIL, NS-100, NS-200, SPPO, B-9, and CA membranes on rinsewaters from copper cyanide, zinc cyanide, acid copper, and chromic acid plating baths. The PA-300 membrane exhibited superior performance for the treatment of copper cyanide, zinc cyanide, and chromic acid rinsewaters, and further development and demonstration of this membrane is recommended. The NS-200 and PBIL membranes exhibited the best performance for treatment of acid copper rinsewaters. Efforts are underway to commercialize all three of the selected membranes (PA-300, NS-200, and PBIL).

INTRODUCTION

Since enactment of the Federal Water Quality Control Act and its amendments, the metal finishing industry has become increasingly concerned with techniques for wastewater treatment. A variety of new technologies have been developed for the treatment of electroplating wastewaters; however, none of these technologies appears to offer an optimum solution to all aspects of the problem. As a result, many platers are waiting for further development and demonstration of new technologies before attempting to make a final decision on the selection of wastewater treatment processes.

Wastewater treatment technologies for the electroplating industry can be broadly classified as end-of-pipe destruction processes or in-plant recovery processes. The end of pipe destruction processes treat a total shop effluent to remove a mixture of heavy metals. At present it is neither technically nor economically feasible to recover and recycle metals from the end-of-pipe processes (1). On the other hand, in-plant recovery processes treat rinsewater from a specific plating bath (or other operation) making it possible to recover and return the heavy metals to the plating bath.

It seems reasonable to speculate that most, if not all, plating shops will require an end-of-pipe treatment process, particularly for diversified job shops where in-plant recovery of all rinsewaters is neither technically nor economically feasible. Even for less diversified shops, end-of-pipe treatment would be required for spills, contaminated plating baths, spent cleaners, etc. However because of the inherent disadvantages of end-of pipe treatment — loss of valuable plating chemicals, cost of sludge disposal, and cost of treatment chemicals — it is also reasonable to speculate that platers will use in-plant recovery processes where the economics for recovery are favorable or where recovery could reduce the load on the end-of-pipe system to the extent necessary to meet the discharge regulations for specific contaminants.

Aside from a few applications in which closed-loop recovery can be achieved by countercurrent rinsing alone, some technique must be used to separate the dissolved plating chemicals from the rinsewater. The leading techniques for making this separation are reverse osmosis (RO), evaporation, and ion exchange. This paper addresses the application of reverse osmosis to the recovery of electroplating rinsewaters with particular emphasis on the performance characteristics of new membrane materials used to treat extreme pH rinsewater.

Principles of Reverse Osmosis

Reverse osmosis is a pressure driven membrane separation process in which a feed stream under pressure (400 - 800 psig) is separated into a purified "permeate" stream and a "concentrate" stream by selective permeation of water through a semi-permeable membrane. There are three major types of commercially available membrane modules: tubular, spiral-wound and hollow-fiber. These are shown in Figure 1. Each of these modules has particular advantages and limitations. Tubular modules are not susceptible to plugging by suspended solids and can be operated at high pressures, but their space requirement (ft^3 per ft^2 membrane surface) is relatively high and their cost is approximately five times as high as the other configurations for an

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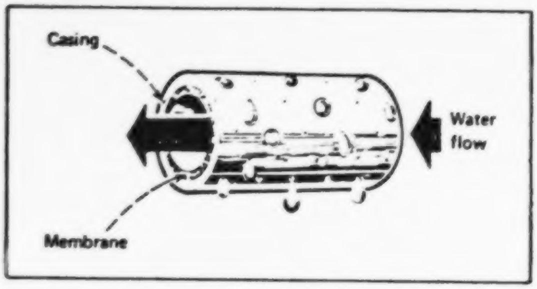
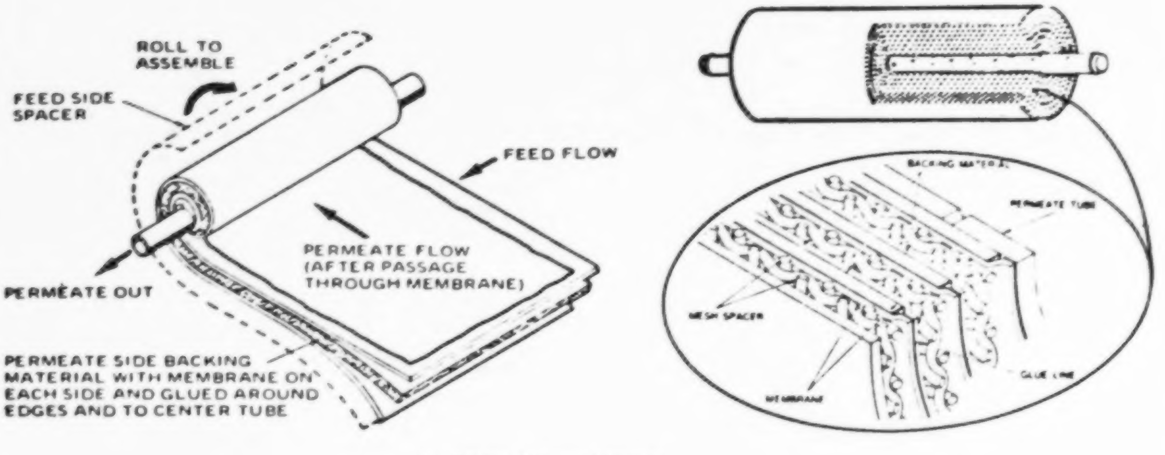
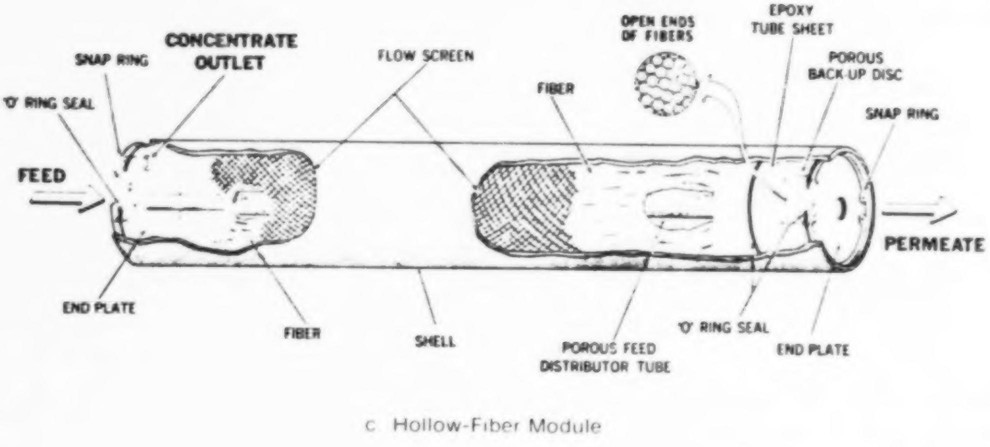

Casing
Water flow
Membrane

a. Tubular Membrane


ROLL TO ASSEMBLE
FEED SIDE SPACER
FEED FLOW
PERMEATE FLOW (AFTER PASSAGE THROUGH MEMBRANE)
PERMEATE OUT
PERMEATE SIDE BACKING MATERIAL WITH MEMBRANE ON EACH SIDE AND GLUED AROUND EDGES AND TO CENTER TUBE
BACKING MATERIAL
PERMEATE TUBE
MESH SPACER
GLUE LINE
MEMBRANE

b. Spiral-Wound Module


CONCENTRATE OUTLET
SNAP RING
'O' RING SEAL
FEED
FLOW SCREEN
OPEN ENDS OF FIBERS
EPOXY TUBE SHEET
POROUS BACK-UP DISC
SNAP RING
FIBER
PERMEATE
END PLATE
FIBER
SHELL
POROUS FEED DISTRIBUTOR TUBE
'O' RING SEAL
END PLATE

c. Hollow-Fiber Module

Figure 1. Membrane Module Configurations

equivalent rate of permeate production. Therefore tubular modules are not recommended for plating applications.

Spiral-wound and hollow-fiber modules are essentially identical in cost for an equivalent rate of permeate production. Hollow-fiber modules have a somewhat lower space requirement per unit of permeate produced; while the spiral-wound modules are less susceptible to plugging by suspended solids.

There are a number of membrane materials presently under development, but only two types are currently in commercial use. The most widely applied is cellulose acetate (or cellulose tri-acetate), which was originally developed for water desalination and has since been adopted for many industrial waste treatment applications. It is available in tubular, spiral-wound, and hollow-fiber configurations and exhibits excellent water permeation rates and high rejection of ionic species. Unfortunately, it is limited to a fairly narrow pH range (2.5 - 7). Operation beyond this range hydrolizes the membrane and destroys its ability to selectively pass water.

The other commercially available membrane is duPont's polyamide membrane which is presently available only in a hollow-fiber configuration. It also exhibits high flux and high rejection, but can be applied over a somewhat broader pH range (4 - 11).

In general the cellulose acetate membrane should be used at low pH, and the polyamide membrane at high pH. In the region of pH overlap neither membrane has an overriding advantage over the other.

Membrane performance is characterized in terms of flux and rejection. The flux is the rate at which purified water permeates through the membrane per unit area of membrane surface and is generally given in gallons per square foot per day (gfd). The rejection of a particular dissolved species is given by:

$$\% \text{ Rejection} = \frac{C_F - C_P}{C_F} \times 100\%$$

where: C_F = concentration in feed stream
C_P = concentration in permeate stream.

In general both flux and rejection increase with operating pressure and decrease with increasing feed concentration. The flux increases with temperature, but rejection is essentially temperature independent. The flow rate of feed tangential to the membrane surface is also an important parameter and must be maintained at a high enough level to prevent the build-up of rejected salts at the membrane surface.

The major advantages and limitations of reverse osmosis are listed in Table I. The objective of the present research effort is to identify new membrane materials that would broaden the allowable pH range (Limitation #1) and would reduce the required frequency of membrane replacement (Limitation #4).

TABLE I
Advantages and Limitations of RO

Advantages

1. Low capital cost. The modular nature of RO units makes them particularly well-suited for small-scale installations.
2. Low energy cost. Only power for pumping is required; there is no phase change as in evaporation.
3. Low labor cost. The process is fully automated and simple to operate requiring little operator attention.
4. Low space requirements. Since RO equipment is compact and operates continuously, it requires minimal tankage.

Limitations

1. There is a limited pH range (about 2.5 - 11) over which current commercially available membranes can operate for extended periods.
2. RO is incapable of concentrating solutions to very high concentrations. For ambient temperature baths a small evaporator is generally required to close the loop.
3. Certain species, e.g., small non-ionized molecules, are not completely rejected by the membrane.
4. Membrane performance generally degrades with time requiring periodic replacement of the membrane modules.

Application of Commercially Available Membranes To Rinsewater Recovery

Because of the potential cost advantage of RO relative to other recovery processes, EPA and AES have sponsored a number of projects aimed at developing and demonstrating RO for the treatment of electroplating rinsewaters. Work performed under AES Project 32 included both in-house and field tests of commercially available membranes (2, 3). The in-house tests were conducted with samples of actual plating baths diluted to various concentrations to simulate actual rinsewater. A total of nine different plating-bath rinsewaters were treated with the two-commercially available membranes (cellulose acetate and polyamide) using full-scale RO modules.

It was concluded from these tests that RO appeared promising for the treatment of nickel baths (Watts, sulfamate, fluoborate) and copper pyrophosphate. Treatment of relatively low-pH cyanide baths also appeared feasible using the polyamide membrane. However, the commercially available membranes did not appear to have a suitable operating life for the treatment of highly oxidizing rinsewaters (chromic acid), low pH (<2) rinsewaters, and high pH (>11) rinsewaters.

Following in-house testing, various field tests were conducted to demonstrate the performance of RO under realistic conditions. The polyamide membrane in hollow fiber configuration was successfully demonstrated for the treatment of Watts nickel rinsewaters (4). (The cellulose acetate membrane in spiral-wound configuration has also been successfully demonstrated on Watts nickel rinsewater (5) as part of AES Project 31.) It was concluded that either of the two commercially available membranes can be used to treat nickel rinsewaters and that the economics for closed-loop nickel recovery can be quite attractive. This has been proven in industrial practice: approximately 100 RO systems have been sold for the treatment of nickel rinsewaters.

In an effort to expand the application of RO to major plating baths other than nickel, two separate field demonstrations were conducted on copper cyanide rinsewaters using the polyamide membrane (6). In general, it was concluded that the polyamide membrane can be used for the recovery of relatively low-pH cyanide rinsewaters provided that the membrane life is adequate. However, since rapid membrane deteriorating was observed in one of the two field tests, the treatment of copper cyanide rinsewaters cannot be considered a proven application.

Based on these results as well as the known pH tolerance of the commercially available membranes, it is evident that new membranes must be developed in order to expand the applicability of RO to major plating baths other than nickel. In particular, membranes must be developed with resistance to pH extremes (<2 and >11) and with resistance to oxidants (chromic acid). To this end AES Project 39 was undertaken, and results from this project are presented and discussed below.

Application of New Membranes to Rinsewater Recovery

During the past two years the Walden Division of Abcor, Inc. has been conducting life tests with various new membrane materials exposed to rinsewaters with both high and low pH and with high levels of oxidants (chromic acid). The objective of this testing program, which was jointly funded by AES and EPA, was to identify new membrane materials which would be applicable to the recovery of a broad range of electroplating rinsewaters.

Materials and Methods

Table 2 lists the membranes investigated during this program along with the manufacturer from which the membrane was obtained and a brief description of the membrane configuration and materials. Membranes other than those listed are under development but, for a variety of reasons, were not submitted by the manufacturer for testing during this program. In addition to the new membrane materials, the two commercially available membrane types, B-9 (polyamide) and CA (cellulose acetate) were tested in order to provide a reference level to which the new membranes could be compared. The B-9 membrane (pH range 4-11) was the reference for alkaline rinsewaters, and the CA membrane (pH range 2.5 - 7) was the reference for acid rinsewaters.

Table 3 lists the plating baths used to prepare the rinsewaters tested in this program. The major components and nominal composition are also listed for each plating bath. These baths were selected because of their extreme pH levels and, in the case of chromic acid, high oxidation potential. Rinsewaters were prepared from each bath of Table 3 by dilution to the appropriate

TABLE 2
Membrane Materials and Configurations Tested

Membrane Material	*Source*	*Description*
PA-300	Fluid Systems Div. of UOP, Inc. San Diego, CA	Flat sheet composite membrane of poly (ether amide) on polysulfone
PBIL	Walden Div., of Abcor, Inc. Wilmington, MA	Flat sheet asymetric membrane of polybenzimidazolone
NS-100	Walden Div., of Abcor, Inc. Wilmington, MA	1/2-inch tubular composite membrane of polyethyleneimine cross-linked with tolylenediisocyanate on polysulfone
NS-200	Fabric Research Lab. Dedham, MA	0.006-inch ID hollow fiber composite membranes of polyfurfuryl alcohol on polysulfone. Modules supplied
SPPO	General Electric Company Wilmington, MA	Flat sheet sulfonated polyphenylene-oxide
B-9	E. I. duPont Wilmington, DE	Hollow-fine-fiber asymetric membranes of aromatic polyamide. Mini-permeator supplied
CA	Abcor, Inc. Wilmington, MA	1/2-inch tubular membrane of asymetric cellulose acetate

TABLE 3
Composition of Plating Baths Tested

Plating Bath	*Component*	*Nominal Composition*
Chromic Acid Udylite	Chromic Acid	34 oz/gal
	Sulfate	0.12 oz/gal
	Catalyst (fluoride)	Unknown
Acid Copper Lea-Ronal	Copper Sulfate	8-12 oz/gal
	Sulfuric Acid	22-28 fl. oz/gal
	Brightener (Copper Gleem PC)	0.4-0.6% Vol.
	Chloride	50 ppm
Copper Cyanide-1 MacDermid	Copper as metal	6.3 oz/gal
	Free Cyanide (as KCN)	2.7 oz/gal
	Potassium Hydroxide	2.0 oz/gal
	Rochelle Salt (Rocheltex)	6% by Vol.
	Brightener (CI Bright Copper)	0.2% by Vol.
	(Potassium Carbonate)	5.0 oz/gal
Copper Cyanide-2 R. O. Hull	Copper as metal	3.75 oz/gal
	Free Cyanide (as NaCN)	1.17 oz/gal
	Caustic	1.17 oz/gal
	Rochell Salt (Roplex)	2-4% by Vol.
	Brightener	none
Zinc Cyanide R. O. Hull	Zinc as metal	2.5-3 oz/gal
	Free Cyanide (as NaCN)	5-7 oz/gal
	Caustic	11-13 oz/gal
	Brightener (ROHCO 532)	0.3 fl. oz/gal

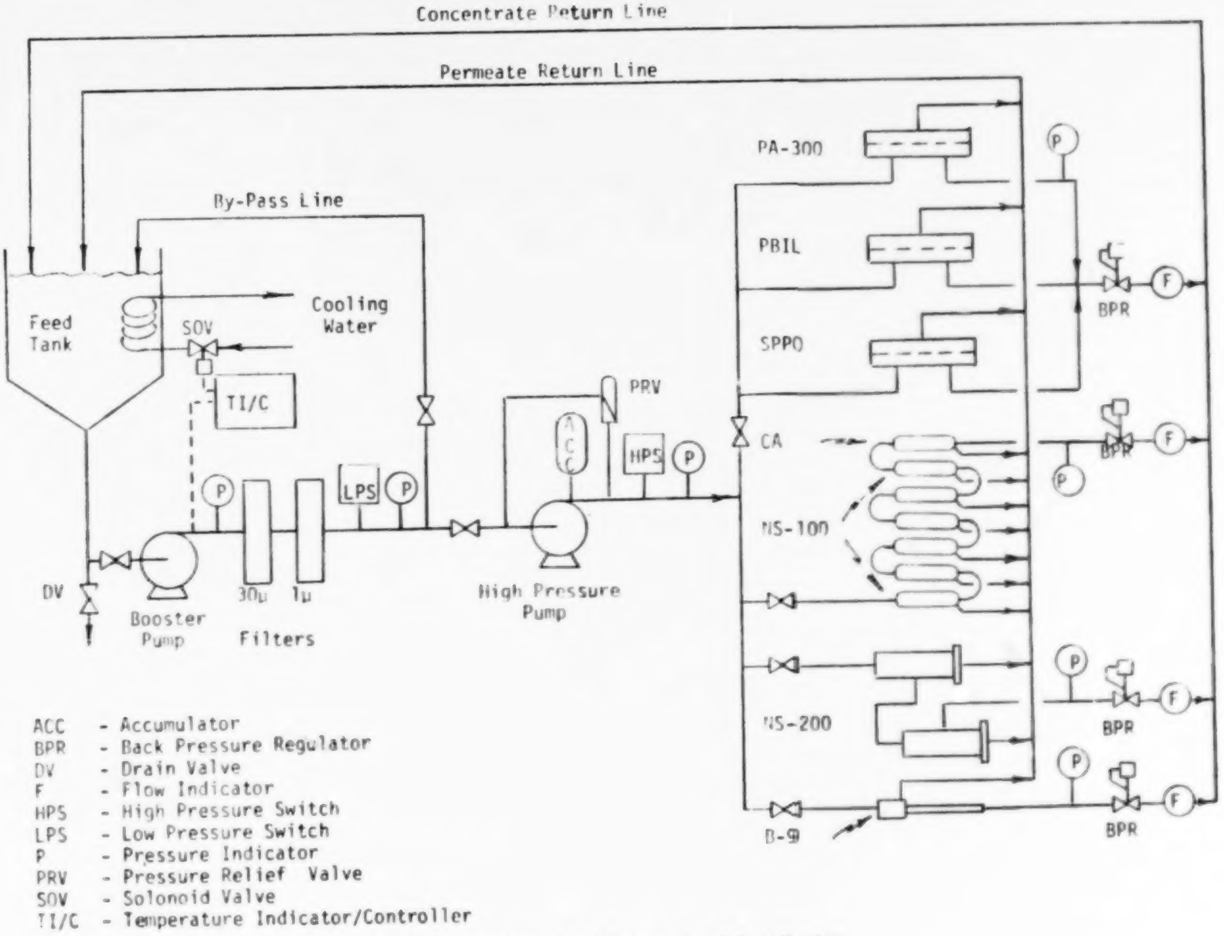

Concentrate Return Line
Permeate Return Line
By-Pass Line
Feed Tank
SOV
Cooling Water
TI/C
DV
Booster Pump
P
30μ
1μ
Filters
LPS
High Pressure Pump
ACC
PRV
HPS
PA-300
PBIL
SPPO
CA
NS-100
NS-200
B-9
BPR
F
ACC - Accumulator
BPR - Back Pressure Regulator
DV - Drain Valve
F - Flow Indicator
HPS - High Pressure Switch
LPS - Low Pressure Switch
P - Pressure Indicator
PRV - Pressure Relief Valve
SOV - Solonoid Valve
TI/C - Temperature Indicator/Controller

Figure 2. Simplified Flow Schematic of Test System

concentration. Life tests were conducted at two dilutions for each bath: 5% of bath strength and 25% of bath strength. The dilutions were performed on a volumetric basis, e.g., one gallon of bath plus three gallons of water for the 25% dilution.

A simplified flow schematic of the test system is shown in Figure 2. Feed was withdrawn from the feed tank by a centrifugal booster pump and passed through two cartridge filters in series. A high-pressure diaphragm pump was used to pressurize the feed and pass it through the membrane test cells. The pressures within the cells were controlled in the range of 400 - 800 psi with back-pressure regulators. An accumulator was used to dampen pressure pulsations from the high-pressure pump, a pressure relief valve and high pressure switch were used to prevent overpressurization of the membranes, and a low pressure switch was used to prevent the pumps from running dry. A cooling coil with automatic temperature control was used to maintain the feed at a constant temperature, and the surface of the feed tank was covered with polyethylene balls to prevent evaporation and CO_2 absorption (by alkaline solutions).

The system was operated in a total recycle mode with both concentrate and permeate returned to the feed tank. This mode of operation permits continuous long-term operation with only a reltively small volume of feed. In general, the membranes were tested at a temperature of 77° F and at the pressures and feed flow rates listed below.

Membrane	*Operating Pressure, psig*	*Feed Circulation Rate, gpm*
PA-300	800	0.3
PBIL	800	0.3
NS-100	600	0.5
NS-200	800	0.5
SPPO	600	---
B-9	400	0.05
CA	600	0.5

Membrane performance was determined by measuring the flux and rejection for each membrane as a function of operating time. The flux was determined by measuring the permeate flow rate (graduate and stopwatch technique) for each membrane, and the rejection was determined by obtaining samples of the feed and the permeate from each membrane analyzing for various bath constituents. Each membrane was operated for 1000 hours on rinsewaters from each of the 4 plating baths—500 hours at 5% of bath strength and 500 hours at 25% of bath strength.

Results and Discussion

Results are presented below for all the plating bath rinsewaters in the orders in which they were tested: copper cyanide, zinc cyanide, acid copper, and chromic acid.

Copper Cyanide

Copper cyanide was the first plating bath to be tested, and during the initial tests the PA-300 and PBIL membranes were not yet available. Therefore the NS-100, NS-200, SPPO, and B-9 membranes were tested using the copper cyanide-1 bath listed in Table 3. The PA-300 and PBIL membranes were tested at a later time using the copper cyanide-2 bath listed in Table 3. These baths are reasonably similar in composition which should permit a direct comparison of the results for all the membranes.

Table 4 gives the results for tests conducted with rinsewater at 5% of bath strength. The performance parameters listed for each membrane are conductivity rejection, copper rejection, free cyanide rejection, and flux. Rejections are given as a percentage of the feed concentration rejected, and flux, for the most part, is given in gallons per square foot of membrane surface per day (gfd). For the hollow fiber modules (NS-200 and B-9) the productivity is reported in cc/min since the exact surface area is difficult to determine and the productivity per unit membrane area is not directly comparable to the flux for flat sheet membranes because of the much higher packing density (ft^2/ft^3) possible with the hollow fiber configuration.

TABLE 4
Membrane Performance During Life Test with Copper Cyanide Rinsewater at 5% of Bath Strength (pH = 10-13)

Membrane	*Performance Parameter*	*Level at 24 Hrs*	*Level at 250 Hrs*	*Level at 500 Hrs*
PA-300	Conductivity Rejection, %	97.5	97.8	97.9
	Copper Rejection, %	99.1	98.0	98.9
	Free Cyanide Rejection, %	98.2	96.7	99.2
	Flux, gfd	15	9	9
PBIL	Conductivity Rejection, %	85.4	90.0	90.5
	Copper Rejection, %	99.3	98.5	98.7
	Free Cyanide Rejection, %	97.2	94.3	98.8
	Flux, gfd	13	8	8
NS-100 (Avg of 5)	Conductivity Rejection, %	90.0	92.5	86.0
	Copper Rejection, %	96.5	96.3	96.0
	Free Cyanide Rejection, %	91.0	90.0	93.0
	Flux, gfd	7	6	6
NS-200 (Avg of 2)	Conductivity Rejection, %	96.2	98.3	88.0
	Copper Rejection, %	99.0	99.8	99.7
	Free Cyanide Rejection, %	96.5	97.0	98.5
	Flux, cc/min	30	32	33
SPPO	Conductivity Rejection, %	96.2	82.0	68.0
	Copper Rejection, %	95.0	92.0	94.0
	Free Cyanide Rejection, %	87.0	80.0	92.0
	Flux, gfd	9	5	4
B-9	Conductivity Rejection, %	96.5	98.3	91.0
	Copper Rejection, %	99.9	99.3	99.4
	Free Cyanide Rejection, %	98.5	97.2	98.7
	Flux, cc/min	1.8	2.2	1.7

The flux and rejections for each membrane are shown at the start of the test, the mid-point, and the end of the test. (Actual sampling times varied slightly from the 24, 250, and 500-hour times shown in this and subsequent tables.) Average results are reported for the NS-100 membrane (five tubes tested in series).

The results of Table 4 indicate that all of the membranes tested exhibited reasonably stable flux and rejection for the 500-hour life test at 5% of bath strength. The apparent drop in conductivity rejection for the NS-100, NS-200, SPPO, and B-9 membranes is believed to be an artifact resulting from the absorption of atmospheric CO_2 which gradually changed the pH of the test solution and shifted the ionic equilibria in the direction of more poorly rejected species. The copper and free cyanide rejections for these same membranes showed no significant decline during the test. In subsequent tests, polyethylene spheres were added to the feed tank to cut down the amount of CO_2 absorption and the pH was more carefully controlled.

In general the PA-300, NS-200, and B-9 membranes gave the highest rejections of conductivity, copper, and free cyanide. Relative to these membranes the PBIL membrane gave equivalent rejections of copper and free cyanide but somewhat lower conductivity rejections. The NS-100 and SPPO membranes gave lower rejections particularly for copper and free cyanide.

The results for the 500 hours life test at 25% of bath strength are given in Table 5. At this concentration the PBIL, NS-200, SPPO, and B-9 membranes showed significant degradation in performance characteristics. For the PBIL membrane the flux decreased to an extremely low level upon exposure to the 25%-of-bath rinsewaters. The rejections are also poor (< 90%) probably as the result of the very low flux. Two NS-200 modules were tested on the 25% rinsewater. Both modules seemed to perform reasonably well until after about 250 hours. After this time one of the modules failed resulting in gross leakage between the feed and permeate sides, and the other module exhibited serious degradation in conductivity, copper, and cyanide rejection. The SPPO membrane exhibited extremely low rejections of all species and rejections decreased with time indicating degradation of the membrane material. For the B-9 membrane the rejections of copper and cyanide declined at a moderate rate, but the flux of the membrane declined rapidly.

Only the PA-300 and NS-100 membranes showed no serious degradation in performance during the tests with the 25%-of-bath rinsewaters. Of these two membranes the PA-300 is clearly superior. The conductivity rejection

TABLE 5
Membrane Performance During Life Test with Copper

Membrane	Performance Parameter	Level at 24 Hrs	Level at 250 Hrs	Level at 500 Hrs
PA-300	Conductivity Rejection, %	96.3	97.0	98.0
	Copper Rejection, %	98.9	99.0	99.3
	Free Cyanide Rejection, %	98.6	99.0	98.8
	Flux, gfd	9	7	8
PBIL	Conductivity Rejection, %	60.6	61.3	56.7
	Copper Rejection, %	89.3	86.4	75.4
	Free Cyanide Rejection, %	87.2	89.6	77.0
	Flux, gfd	0.8	0.7	0.9
NS-100 (Avg of 5)	Conductivity Rejection, %	75.0	76.0	78.5
	Copper Rejection, %	92.3	90.0	87.0
	Free Cyanide Rejection, %	92.5	90.8	90.2
	Flux, gfd	5	5	5
NS-200 (Avg of 2)	Conductivity Rejection, %	75.0	76.5	30.0
	Copper Rejection, %	99.4	96.8	32
	Free Cyanide Rejection, %	97.0	95.5	27
	Flux, cc/min	25	30	(Failure)
SPPO	Conductivity Rejection, %	30	23	22
	Copper Rejection, %	55	37	30
	Free Cyanide Rejection, %	67	61	35
	Flux, gfd	10	8	4
B-9	Conductivity Rejection, %	77	80	80
	Copper Rejection, %	99.0	96.7	94.1
	Free Cyanide Rejection, %	98.3	95.3	92.0
	Flux, cc/min	0.6	0.2	0.1

TABLE 6
Membrane Performance During Life Test with Zinc Cyanide Rinsewater at 5% of Bath Strength (pH = 12-13)

Membrane	Performance Parameter	Level at 24 Hrs	Level at 250 Hrs	Level at 500 Hrs
NS-100 (Avg of 5)	Conductivity Rejection, %	72	75	81
	Zinc Rejection, %	--	97.7	96.8
	Free Cyanide Rejection, %	88	92.7	91.0
	Flux, gfd	7	6	6
NS-200 (Avg of 2)	Conductivity Rejection, %	67	60	67
	Zinc Rejection, %	--	99.7	99.2
	Free Cyanide Rejection, %	96.8	95.4	91.0
	Flux, cc/min	100	105	97
SPPO	Conductivity Rejection, %	25	30	41
	Zinc Rejection, %	--	72	73
	Free Cyanide Rejection, %	50	63	53
	Flux, gfd	7	6	6
B-9	Conductivity Rejection, %	73	81	83
	Zinc Rejection, %	--	99.9	99.9
	Free Cyanide Rejection, %	97.2	98.5	97.7
	Flux, cc/min	1.1	1.0	0.75

TABLE 7
Membrane Performance During Life Test with Zinc Cyanide Rinsewater at 25% of Bath Strength (pH > 13)

Membrane	Performance Parameter	Level at 24 Hrs	Level at 250 Hrs	Level at 500 Hrs
PA-300	Conductivity Rejection, %	87	87	87
	Zinc Rejection, %	99.1	--	99.3
	Free Cyanide Rejection, %	97.3	--	97.0
	Flux, gfd	17	14	13
PBIL	Conductivity Rejection, %	35	41	52
	Zinc Rejection, %	--	--	96
	Free Cyanide Rejection, %	--	--	91
	Flux, gfd	1.1	1.1	0.9
NS-100 (Avg of 6)	Conductivity Rejection, %	42	43	42
	Zinc Rejection, %	87	91	82
	Free Cyanide Rejection, %	78	88	77
	Flux, gfd	4	10	10
NS-200 (Avg of 2)	Conductivity Rejection, %	33	20	31
	Zinc Rejection, %	93.0	95.0	93.5
	Free Cyanide Rejection, %	80	88	82
	Flux, cc/min	75	92	75
SPPO	Conductivity Rejection, %	33	20	35
	Zinc Rejection, %	50	46	56
	Free Cyanide Rejection, %	57	41	31
	Flux, gfd	6	6	2
B-9	Conductivity Rejection, %	30	5	53
	Zinc Rejection, %	98.1	98.0	95.5
	Free Cyanide Rejection, %	90.0	95.0	91.3
	Flux, cc/mn	0.12	(.9)	0.10

was quite good, the copper and free cyanide rejections were excellent, and the flux was high. Both flux and rejection were stable throughout the test. On the other hand the NS-100 rejections were rather poor and the flux was only moderate. It is concluded that, for the treatment of copper cyanide rinsewaters, the PA-300 is the best of the membranes tested.

Zinc Cyanide

Following the tests with copper cyanide rinsewaters at 25% of bath strength, the NS-200 modules were replaced with two new modules, and a new B-9 mini-permeator was installed. The NS-100 and SPPO membranes were not changed prior to the zinc cyanide tests. The PA-300 and PBIL membranes were not obtained in time for the zinc cyanide tests at 5% of bath strength but were tested at 25% of bath strength.

Table 6 gives the results for the test with the 5%-of-bath rinse-water. All of the membranes tested appeared to be reasonably stable at this rinsewater concentration, and the commercially available B-9 membrane appeared to have the highest overall rejections. The low rejections for the SPPO membrane were probably the result of membrane deterioration during testing with 25%-of-bath copper cyanide rinsewater.

Results for the life-test with 25%-of-bath zinc cyanide rinsewater are given in Table 7. Again, all of the membranes tested exhibited reasonably stable performance. However, except for the PA-300 membrane the flux and/or rejections of the membranes were too low for cost-effective recovery of zinc cyanide rinsewaters at this concentration. The low conductivity rejections (generally < 50% except fot the PA-300 membrane) could be the result of the high concentration of hydroxide ion (which is difficult to reject) in the zinc cyanide rinsewaters. The PA-300 membrane, by contrast, gave excellent zinc and free cyanide rejections and a conductivity rejection much higher than for any of the other membranes. In addition the flux for the PA-300 was quite high and appeared to be leveling off at a stable value of about 12 gfd. Based on these data it is concluded that, for the treatment of zinc cyanide rinsewaters, the PA-300 is the best of the membranes tested.

Acid Copper

Following the tests with the zinc cyanide rinsewater at 25% of bath strength, new PA-300 and PBIL membranes were installed in the system; however, the NS-100 and NS-200 membranes were not changed since new samples of these membranes were not available. The SPPO membrane was replaced prior to the test at 25% of bath strength, but during initial characterization tests with a sodium chloride solution, it was discovered that the new SPPO membrane was giving very poor rejections (<60%). This membrane was therefore eliminated from the test program. The B-9 membrane, which served as a reference membrane for alkaline solutions, was replaced by a CA reference membrane for tests with acid copper and chromic acid solutions. However the CA membrane was not installed in the test system until after the test with 5%-of-bath acid copper rinsewater.

Results are shown in Table 8 for the life test with acid copper rinsewater at 5% of bath strength. The PBIL membrane exhibited exceptionally high rejections for all species including conductivity (rejection >99%), and the rejection appeared to be stable. Although the flux (~ 4 gfd) is rather low, it is believed that membranes with a higher flux could be prepared by varying the casting procedure. (This membrane was still in the process of being optimized when the test sample of membrane was obtained.) The NS-200 membrane also exhibited quite good performance characteristics during this test. Both the flux and rejection for this membrane appear adequate for successful application to copper sulfate rinsewaters. The PA-300 membrane gave a lower level of performance, and the NS-100 performed poorly in this test. It is possible that the copper ions in the rinsewater complexed with amine groups on the NS-100 membrane surface (and to a lesser extent on the PA-300 surface) resulting in poor rejection performances.

TABLE 8
Membrane Performance During Life Test with Acid Copper Rinsewater at 5% of Bath Strength (pH = 1.2)

Membrane	*Performance Parameter*	*Level at 24 Hrs*	*Level at 250 Hrs*	*Level at 500 Hrs*
PA-300	Conductivity Rejection, %	79.7	89.2	82.6
	Copper Rejection, %	99.7	--	--
	Sulfate Rejection, %	92.9	--	94.8
	Flux, gfd	32	23	14
PBIL	Conductivity Rejection, %	99.4	99.1	99.5
	Copper Rejection, %	>99.9	--	--
	Sulfate Rejection, %	99.8	--	98.0
	Flux, gfd	3.6	7.2	4.0
NS-100 (Avg of 6)	Conductivity Rejection, %	20.0	50.0	24.2
	Copper Rejection, %	94.7	--	--
	Sulfate Rejection, %	49.8	--	57.1
	Flux, gfd	11	16	19
NS-200 (Avg of 2)	Conductivity Rejection, %	97.2	97.2	96.0
	Copper Rejection, %	99.9	--	--
	Sulfate Rejection, %	98.7	--	98.1
	Flux, cc/min	43	38	31

TABLE 9
Membrane Performance During Life Test With Acid Copper Rinsewater at 25% of Bath Strength (pH = 0.6-0.9)

Membrane	*Performance Parameter*	*Level at 24 Hrs*	*Level at 250 Hrs*	*Level at 500 Hrs*
PA-300	Conductivity Rejection, %	78.1	82.6	90.0
	Copper Rejection, %	99.9	>99.9	>99.9
	Sulfate Rejection, %	76.5	92.2	83.0
	Flux, gfd	12	6	3.6
PBIL	Conductivity Rejection, %	99.2	98.3	99.1
	Copper Rejection, %	>99.9	>99.9	>99.9
	Sulfate Rejection, %	99.3	98.1	94.4
	Flux, gfd	3.9	2.5	2.8
NS-100 (Avg of 5)	Conductivity Rejection, %	26.7	31.5	47.2
	Copper Rejection, %	98.2	98.3	96.0
	Sulfate Rejection, %	1.6	60.4	50.9
	Flux, gfd	14.4	7.2	4.7
NS-200 (1 of 2)	Conductivity Rejection, %	86.[illegible]	84.8	91.3
	Copper Rejection, %	97.8	98.5	99.0
	Sulfate Rejection, %	86.1	91.2	94.9
	Flux, cc/min	25	17	18.5
CA	Conductivity Rejection, %	92.3	57.8	39.1
	Copper Rejection, %	99.9	97.2	83.3
	Sulfate Rejection, %	92.0	74.9	49.2
	Flux, gfd	4.7	8.7	9.8

For all membranes the rejections remained stable with operating time, but significant declines in flux were observed for the PA-300 and NS-200 membranes. Results for copper rejection are incomplete because of immersion deposition of copper on various stainless steel components within the test system. Copper concentrations in the feed solution decreased to very low levels following the first analysis at 24 hours.

Results are shown in Table 9 for the life test with acid copper rinsewater at 25% of bath strength. Immersion deposition was not a problem during this test since significant deposition had already occurred in the previous test, and copper concentrations in the feed were much higher. Again the PBIL membrane exhibited extremely high rejection of all species, but the flux was low. The flux and rejections were reasonably stable for the duration of the test with the exception of sulfate rejection. The NS-200 membrane declined in performance relative to the test at 5% of bath strength, but is still considered adequate for successful application of this membrane particularly in view of the fact that this same membrane had been used during the zinc cyanide life tests. The rejection of conductivity, copper, and sulfate increased during the test, and the flux appeared to stabilize after an initial decline. The PA-300 membrane exhibited excellent copper rejections, but the sulfate and conductivity rejections were low. The PA-300 rejections generally increased with operating time but the flux decreased substantially during the life test to only one-third of its initial value. The NS-100 membranes exhibited very poor but stable rejections and a substantial decrease in flux over the duration of the test. The CA membrane was degraded by acid hydrolysis at the low pH of the rinsewater. This deterioration is evidenced by a substantial loss in rejection with a simultaneous increase in flux.

On the basis of the life tests with acid copper rinsewaters, it is concluded that the NS-200 and PBIL membranes exhibit the best performance characteristics.

Chromic Acid

Following the tests with acid copper, new PA-300 and PBIL membranes were installed in the test system, but the same NS-100 and NS-200 membranes were retained. Only one NS-100 tube and one NS-200 module were tested on the 5%-of-bath chromic acid rinsewater. For the test at 25% of bath strength, the NS-200 was discontinued because of severe membrane degradation.

Results of the life test at 5% of bath strength are shown in Table 10. Of the membranes tested only the PA-300 and PBIL gave stable performance. For the NS-100, NS200, and CA membranes, the rejections decreased, and the flux levels increased with operating time. This behavior is indicative of chemical degradation of the membrane surfaces.

Both the PA-300 and the PBIL membranes gave exceptionally stable flux and rejection performance throughout the life test. Of these two membranes, the PA-300 exhibited better performance for both flux and rejection.;

The results for the life test with chromic acid at 25% of bath strength are shown in Table 11. The NS-100 and CA membranes degraded quite rapidly, and the evaluation of these membranes had to be discontinued shortly after the life test was initiated. The PBIL was operated for the entire 600-hour test but the rejections of both conductivity and hexavalent chrome declined substantially. On the other hand the PA-300 membrane exhibited very good conductivity rejection and excellent chromium rejection during the entire life test. Although the flux is low it appeared to be reasonably stable. It is believed that the PA-300 could be used to economically recover chromic acid rinsewater in spite of the low flux because of the relatively high value of the recovered chemicals.

It is concluded that, of the membranes tested, the PA300 is the only one that is suitable for the treatment of chromic acid rinsewater.

TABLE 10
Membrane Performance During Life Test
With Chromic Acid Rinsewater at 5% of Bath Strength
(pH = 1.3-1.7)

Membrane	*Performance Parameter*	*Level at 24 Hrs*	*Level at 250 Hrs*	*Level at 500 Hrs*
PA-300	Conductivity Rejection, %	97.9	97.8	97.5
	Chromium (VI) Rejection, %	98.8	98.9	98.6
	Flux, gfd	8	10	9
PBIL	Conductivity Rejection, %	95.0	95.0	94.1
	Chromium (VI) Rejection, %	96.8	96.6	96.3
	Flux, gfd	3.8	7.2	8.6
NS-100	Conductivity Rejection, %	43.3	23.1	22.7
	Chromium (VI) Rejection, %	51.0	42.9	67.4
	Flux, gfd	10	36	44
NS-200	Conductivity Rejection, %	28.3	0.0	0.0
	Chromium (VI) Rejection, %	25.8	11.4	18.0
	Flux, cc/min	17	140	150
CA	Conductivity Rejection, %	96.2	88.5	31.8
	Chromium (VI) Rejection, %	97.3	91.4	42.0
	Flux, gfd	11	27	60

TABLE 11
Membrane Performance During Life Test
With Chromic Acid Rinsewater at 25% of Bath Strength
(pH = 1.1-1.2)

Membrane	*Performance Parameter*	*Level at 24 Hrs*	*Level at 300 Hrs*	*Level at 600 Hrs*
PA-300	Conductivity Rejection, %	95.9	97.3	97.5
	Chromium (VI) Rejection, %	97.9	99.1	98.8
	Flux, gfd	5.4	2.5	3.1
PBIL	Conductivity Rejection, %	92.2	77.7	73.3
	Chromium (VI) Rejection, %	96.1	90.8	83.4
	Flux, gfd	4.0	2.8	5.1
NS-100	Conductivity Rejection, %	15.7	(Test Discontinued)	
	Chromium (VI) Rejection, %	33.2		
	Flux, gfd	42.3		
CA	Conductivity Rejection, %	75.3	(Test Discontinued)	
	Chromium (VI) Rejection, %	85.7		
	Flux, gfd	21.6		

Conclusions

The results of the life tests described above indicate that the PA-300 is the most promising of all the membranes tested for the treatment of rinsewaters with extreme pH levels or high levels of oxidants (chromic acid). The PA-300 membrane was clearly superior to the other membranes for treatment of copper cyanide, zinc cyanide, and chromic acid rinsewaters. However the NS200 and PBIL membranes proved to be better than the PA-300 for the treatment of acid copper rinsewaters.

Of these three membranes, the PA-300 is the closest to commercialization. A full-scale, spiral-wound, membrane module containing the PA-300 membrane has been developed and extensively tested by the Fluid System Division of UOP for brackish- and seawater desalting. Although the module has not yet been officially commercialized, modules are being fabricated and supplied on a special-order basis. The manufacturer is currently working on an order to supply a large number of 6-inch diameter PA-300 modules for a Saudi Arabian desalting plant.

The NS-200 membrane is being actively developed toward commercialization by the Fabric Research Laboratory. At present, hollow-fiber modules with an output of 100-300 gallons per day (approximately one-tenth the output of a full-scale module) are being fabricated for testing on seawater desalination and various wastewater streams. The manufacturer anticipates commercialization within one year.

The PBIL membrane is being developed by the Walden Division of Abcor, Inc. under contract to OWR&T. Membrane casting procedures have been optimized, and a program has been recently initiated to develop procedures for fabricating the PBIL membrane in a spiral-wound configuration.

Future Work

Before the PA-300 or any other membranes can be offered to the plater as a viable means of achieving closed-loop recovery of rinsewaters, the membrane must be demonstrated on actual rinsewater under practical operating conditions. A new program, jointly funded by EPA (Grant No. R805300010) and AES (Research Project No. 45), has been initiated to demonstrate the performance of new RO membranes for closed-loop treatment of rinsewaters, this program will include fabrication of a full-scale mobile RO system with an evaporator to permit closed-loop treatment of ambient temperature plating baths. The system will be fitted with PA-300 spiral-wound modules, and recovery of zinc cyanide rinsewaters will be demonstrated at New England Plating Co.

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Corrosion-Resistant Coatings With Low Water Pollution Potential

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ABSTRACT

Results obtained to date under this program have shown that many of the new, currently available, less polluting corrosion-protection systems are viable alternatives to currently used more polluting systems. Selection of a specific system for use in a given application would depend on the corrosion-protection requirements for the product being manufactured. Many of the systems selected for final evaluation and characterization in this program can provide corrosion protection equivalent to or superior to that for currently used systems. These new corrosion-protection systems also offer additional benefits such as less waste treatment, increased operational safety, lower energy consumption, longer service life and greater production output.

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INTRODUCTION

Protection of metallic components from corrosive attack is of major importance in the aerospace and metalworking industries. This protection is necessary to maximize the life-cycle of metallic parts. Protective coatings are the most effective means in terms of weight and cost for providing protection against galvanic and atmospheric corrosion. Many coatings that are currently in use, however, are formulated from toxic chemicals which, if not properly treated and controlled, can induce damaging effects in the environment. Mounting concern over environmental pollution and more stringent EPA and OSHA regulations have applied pressure on metal-finishers to consider new less polluting, corrosion-protection systems in lieu of currently used organic solvent paint systems and cyanide electroplating systems.

Under U. S. Environmental Protection Agency (EPA)

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Grant No. R804331, entitled "Evaluation of Reduced-Pollution, Corrosion-Protection Systems," Grumman is conducting a program to evaluate low-polluting, corrosion-protection systems and to demonstrate that these systems are viable alternatives to currently used, higher polluting coatings. The following types of systems have been evaluated as potential alternatives to those now being used.

- Water-borne paints in place of organic solvent coatings
- Non-cyanide cadmium plating in place of cyanide cadmium plating
- Non-cyanide copper plating in place of cyanide copper plating
- Mechanical plating in place of cyanide cadmium plating
- Spray-and-bake aluminum coatings in place of cyanide cadmium plating
- Fluidized bed/powder spray coatings in place of organic solvent coatings
- Trivalent chromium plating in place of hexavalent chromium plating
- Ion vapor deposition (IVD) of aluminum in place of cyanide cadmium plating.

Where possible, several candidate coating systems were selected for evaluation in each of these areas. Based on preliminary screening tests, one system of each type was selected for additional testing. The results of these tests have shown that many of these coating types can provide protection equivalent to that of higher polluting systems in certain applications. In addition to determining performance criteria, economic and process requirements have also been considered. The results of these evaluations are summarized in Table 1.

Alternatives to Organic Solvent Paints

Water-borne paints and powder coatings were evaluated as potential alternatives to organic solvent paints. The need for replacement of these coatings, which have widespread applications, arises from the toxicity of the solvents used. Additional problems such as

TABLE 1. EVALUATION OF REDUCED-POLLUTION CORROSION-PROTECTION SYSTEMS

REDUCED-POLLUTION CORROSION-PROTECTION SYSTEM	CURRENTLY USED SYSTEM	TYPICAL APPLICATIONS	SELECTED SYSTEMS	APPLICATION PROCEDURE	PERFORMANCE RELATIVE TO CURRENTLY USED SYSTEM*	EQUIPMENT COST RELATIVE TO CURRENTLY USED SYSTEM		
						FOR NEW INSTALLATION	FOR CONVERSION OF OLD EQUIPMENT	POLLUTION CONTROL & WASTE TREATMENT
WATER-BORNE PAINTS	ORGANIC SOLVENT PAINTS	AIRCRAFT SKINS, RIBS AND FITTINGS, SCREW MACHINE PRODUCTS, HARDWARE.	GLIDDEN AQUALURE 634-W-804	SPRAY-OVEN CURE	VERY GOOD FOR MODERATE SERVICE CONDITIONS**	SLIGHTLY HIGHER (CURING OVENS REQ'D)	MINIMAL CHANGE OVER COSTS (CURING OVENS REQ'D)	MAJOR PORTION OF WASTE TREATMENT & POLLUTION CONTROL COSTS ELIMINATED
			STERLING-LACQUER AQUATHANE II	SPRAY-AIR DRY		EQUIVALENT	MINIMAL CHANGE OVER COSTS	
NON-CYANIDE CADMIUM	CYANIDE CADMIUM	AIRCRAFT BULKHEADS, LANDING GEARS AND WING FOLD MECHANISMS	LEA-RONAL KADIZID	ELECTROPLATING	EXCELLENT	EQUIVALENT	MINIMAL CHANGE OVER COSTS (LINE TANKS)	CYANIDE TREATMENT STEP ELIMINATED
NON-CYANIDE COPPER	CYANIDE COPPER	AIRCRAFT BULKHEADS, LANDING GEARS AND WING-FOLD MECHANISMS	ENTHONE ENTHOBRITE CU-942	ELECTROPLATING	EXCELLENT	EQUIVALENT	MINIMAL CHANGE OVER COSTS (LINE TANKS)	CYANIDE TREATMENT STEP ELIMINATED
MECHANICAL PLATING	CYANIDE CADMIUM	AIRCRAFT LANDING GEARS, FITTINGS AND FASTENERS	3M TRANSIFLO	TUMBLING WITH CHEMICALS & BRASS BEADS	EXCELLENT	MEDIUM	NEW EQUIPMENT REQUIRED	CYANIDE TREATMENT STEP ELIMINATED
SPRAY AND BAKE ALUMINUM COATINGS	CYANIDE CADMIUM	AIRCRAFT ARRESTING HOOKS AND WING FOLD MECHANISMS	TIODIZE ALUMAZITE Z	SPRAY-OVEN CURE	VERY GOOD	LOW–MEDIUM	NEW EQUIPMENT REQUIRED	SOLVENT RECOVERY SYSTEM REQUIRED; WASTE TREATMENT COSTS ELIMINATED
FLUIDIZED BED/POWDER SPRAY COATINGS	ORGANIC SOLVENT PAINTS	HOOKS, CLAMPS, HOISTING ASSEMBLIES, BATTERY BOXES AND CABLES, TORQUE WRENCHES, METAL TOYS	NYLON	FLUIDIZED BED; ELECTROSTATIC POWDER SPRAY	EXCELLENT	MEDIUM	NEW EQUIPMENT REQUIRED	DUST CONTROL EQUIPMENT REQUIRED; WASTE TREATMENT COSTS ELIMINATED
TRIVALENT CHROMIUM PLATING	HEXAVALENT CHROMIC ACID PLATING	AUTOMOBILE BUMPERS, APPLICANCE PARTS, DECORATIVE PARTS	HARSHAW TRICHROME	ELECTROPLATING	VERY GOOD	EQUIVALENT	MINIMAL CHANGE OVER COSTS (LINE TANKS)	CHROME REDUCTION STEP ELIMINATED
IVD ALUMINUM	CYANIDE CADMIUM	AIRCRAFT FASTENERS AND FITTINGS	McDONNELL AIRCRAFT IVADIZE	ION VAPOR DEPOSITION	EXCELLENT	HIGH	NEW EQUIPMENT REQUIRED	MAJOR PORTION OF WASTE TREATMENT & POLLUTION CONTROL COSTS ELIMINATED

*EXCELLENT – EQUIVALENT OR SUPERIOR TO CURRENTLY USED SYSTEM, GOOD FOR HIGH PERFORMANCE APPLICATIONS
VERY GOOD – EXCEEDS SPECIFICATIONS OF CURRENTLY USED SYSTEM. (BASED ON MIL SPECS MIL-C-81773 "COATING, POLYURETHANE, ALPHATIC, WEATHER RESISTANT", MIL-C-14550 "COPPER PLATING (ELECTRODEPOSITED), AND FEDERAL SPECIFICATIONS QQ-C-3320 "CHROMIUM PLATING (ELECTRODEPOSITED, QQ-P-416 "PLATING, CADMIUM ELECTRODEPOSITED)

**MAY REQUIRE FURTHER DEVELOPMENT FOR SEVERE SERVICE APPLICATIONS SUCH AS IN MIL-C-81773 flammability, rising prices and decreasing availability of solvents emphasize the need for replacement. Use of either water as the volatile component or 100% solid resin systems virtually eliminates these problems.

Seven water-borne paint systems and three powder coatings were evaluated. The water-borne paints were divided into two groups: air-drying and oven-curing (Table 2). These were applied to pretreated (solvent clean, alkaline clean, deoxidize and alodine) 2024-T3 aluminum panels according to manufacturers recommendations. Water-borne primers supplied with the paints were used. Several of the paints were also tested with an organic solvent epoxy primer. The powder coatings were applied to aluminum and steel panels by electrostatic powder spray. One of the powder coatings was also applied using a fluidized bed.

Results of the screening tests for the water-borne paints and powder coatings are shown in Tables 3 and 4. An air-drying system (Aquathane II with organic solvent epoxy primer) and an oven-curing system (Aqualure 634-W-804 with Aqualure primer) were selected for further testing. These systems provided the best adhesion, flexibility, and impact resistance of the water-borne paints tested. The organic solvent epoxy primer was used with Aquathane II to improve adhesion over that offered by the Aquathane primer. The nylon and epoxy powder coatings were found to provide excellent performance in screening tests. The polyester powder coating did not provide good impact resistance or flexibility.

Final characterization tests (Table 5) show that the nylon powder coatings provide better hydrolytic fluid resistance and hydrolytic stability than the other coatings tested. Of the water-borne paints, the oven-curing system (Aqualure 634-W-804) showed slightly better hydraulic stability. Differences in other properties, such as extended outdoor weathering resistance (under test), that could influence the coating choice for a specific application may also be apparent.

The decision to use a specific coating or coating type must be based on other factors in addition to performance for each specific application. For example, equipment requirements are such that the air-drying water-borne paints can replace organic solvent paints directly in existing applications if the performance requirements can be met. The oven-curing systems will require the installation of curing ovens, which may be justified if additional performance can be obtained from these systems. Both the air-drying and oven-curing water-borne paints eliminate the need for organic solvent pollution control equipment. Powder coatings require installation of new equipment, either fluidized bed or electrostatic powder spray, which is amenable to automation. Both types of powder application can provide high resin utilization. Although dust control equipment is needed for powder coating systems, organic solvent pollution control equipment is not required. In addition, powder coatings eliminate solvent compatibility problems, and allow resins such as nylon to be used as protective coatings.

Alternatives to Cyanide Copper Plating

Non-cyanide copper electroplating solutions were evaluated as potential alternatives to cyanide copper plating solutions. Cyanide toxicity and waste treatment requirements present good reasons for its replacement. Several non-cyanide copper plating systems are currently available. The following cyanide-free systems were

TABLE 2. WATER-BORNE PAINT SYSTEMS EVALUATED

PAINT SYSTEM	MANUFACTURER	TYPE	CURE	PRIMER*
AQUATHANE WA-1001	STERLING LACQUER	EPOXY-ACRYLIC	AIR DRY	AQUATHANE WA1017
AQUATHANE II	STERLING LACQUER	URETHANE	AIR DRY	AQUATHANE WA1017
AQUALURE 481-W-02114	GLIDDEN	ACRYLIC	149°C (300°F) – 15 MIN	AQUALURE 631-L-128 (ACRYLIC)
AQUALURE 634-W-804	GLIDDEN	POLYESTER	177°C (350°F) – 15 MIN	AQUALURE 631-L-128 (ACRYLIC)
SAF-T-300-W-39	U.S. PAINT, LACQUER, & CHEMICAL	EPOXY	AIR DRY	SAF-T-300-G-19A
SAF-T-300-W-44	U.S. PAINT, LACQUER, & CHEMICAL	URETHANE	AIR DRY	SAF-T-300-G-19A
CARBOSET 514H/ EPON 828 FORMULATION	BF GOODRICH RESIN/ SHELL RESIN	EPOXY-ACRYLIC	149°C (300°F) – 15 MIN	NONE REQUIRED

*EPOXY PRIMER MIL-P-23377C MAY ALSO BE COMPATIBLE WITH EACH OF THESE SYSTEMS

TABLE 3. RESULTS OF SCREENING TESTS OF WATER-BORNE PAINT SYSTEMS

SYSTEM*	PRIMER SURFACE APPEARANCE	PRIMER ADHESION	PRIMER WASTE RESISTANCE	TOPCOAT SURFACE APPEARANCE	GLOSS (60°)	TOPCOAT ANCHORAGE	TOPCOAT COATING ANCHORAGE	TOPCOAT FLEXIBILITY	TOPCOAT IMPACT RESISTANCE	TOPCOAT HEAT RESISTANCE	TOPCOAT LUBE OIL RESISTANCE
CONTROL EPOXY PRIMER POLYURETHANE TOPCOAT	SATISFACTORY	GOOD	SLIGHT DISCOLORATION**; NO OTHER DEFECT	VERY SLIGHT MOTTLING	89	GOOD	GOOD	PASS	PASS – 5.4 JOULES (48 IN. LB.)	NO FILM DEFECTS; VERY SLIGHT DISCOLORATION**	NO FILM DEFECTS; SLIGHT DISCOLORATION**
AQUATHANE WA 1017 PRIMER WA 1001 TOPCOAT	SATISFACTORY	GOOD	DISCOLORATION**; NO OTHER DEFECT	GOOD	73	GOOD	GOOD	FAIL-FILM CRACKING	FAIL – 2.3 JOULES (20 IN. LB.)	NO FILM DEFECTS; SLIGHT DISCOLORATION**	NO FILM DEFECTS; SLIGHT DISCOLORATION**
EPOXY PRIMER AQUATHANE II TOPCOAT	SATISFACTORY	GOOD	SLIGHT DISCOLORATION**; NO OTHER DEFECT	SLIGHT MOTTLING	54	GOOD	GOOD	PASS	PASS – 5.4 JOULES (48 IN. LB.)	NO FILM DEFECTS; DISCOLORATION**	NO FILM DEFECTS; DISCOLORATION**
AQUATHANE WA 1017 PRIMER AQUATHANE II TOPCOAT	SATISFACTORY	GOOD	DISCOLORATION**; NO OTHER DEFECT	VERY SLIGHT MOTTLING	58	POOR ADHESION-BLISTERING	GOOD	PASS	PASS – 5.4 JOULES (48 IN. LB)	NO FILM DEFECTS; DISCOLORATION**	NO FILM DEFECTS; HEAVY DISCOLORATION**
AQUALURE 631 L 128 PRIMER*** 481 W 02114 TOPCOAT***	SATISFACTORY (ORANGE PEEL EFFECT)	GOOD	VERY SLIGHT FILM SOFTENING	ORANGE PEEL EFFECT SURFACE NOT LEVEL	29	GOOD	GOOD	FAIL-FILM CRACKING	FAIL – 2.3 JOULES (20 IN. LB)	NO FILM DEFECTS; V. SLIGHT DISCOLORATION**	SLIGHT FILM SOFTENING; SLIGHT DISCOLORATION**
AQUALURE 631 L 128 PRIMER*** 634 W 804 TOPCOAT***	SATISFACTORY (ORANGE PEEL EFFECT)	GOOD	VERY SLIGHT FILM SOFTENING	GOOD	80	GOOD	GOOD	PASS	PASS – 5.4 JOULES (48 IN. LB)	NO FILM EFFECTS; V. SLIGHT DISCOLORATION**	FILM SOFTENING SLIGHT DISCOLORATION**
SAF T 300G 19A PRIMER SAF T 300W 39 TOPCOAT	SATISFACTORY	FAIL PRIMER LIFTED FROM SUBSTRATE	FAIL-FILM SOFTENED	MOTTLING	68	FAIL - TOPCOAT & PRIMER LIFTED FROM SUBSTRATE	GOOD	FAIL-FILM CRACKING	FAIL – 2.3 JOULES (20 IN. LB)	NO FILM DEFECTS; DISCOLORATION**	NO FILM DEFECTS SOME DISCOLORATION
SAF T 300G 19A PRIMER SAF T 300W 44 TOPCOAT	SATISFACTORY	FAIL PRIMER LIFTED FROM SUBSTRATE	FAIL FILM SOFTENED	GOOD	55	FAIL - TOPCOAT LIFTED FROM PRIMER	POOR - FILM SEPARATED FROM PRIMER	PASS	PASS – 5.4 JOULES (48 IN. LB)	NO FILM DEFECTS; SLIGHT DISCOLORATION**	FILM SOFTENING; DISCOLORATION**
CARBOSET 514H EPON 828 FORMULATION TOPCOAT***				ORANGE PEEL EFFECT; SURFACE NOT LEVEL	100	GOOD	GOOD	PASS	FAIL – 2.3 JOULES (20 IN. LB)	NO FILM DEFECTS	SLIGHT FILM SOFTENING (TACKY); SLIGHT DISCOLORATION**

*ALODINE PRETREATMENT
**NOT CAUSE FOR REJECTION
***BAKE CURE SYSTEMS

evaluated and compared to MacDermid's Rocheltex cyanide copper plating system:

- Cu-Pure - Lea-Ronal, Inc.
- Enthobrite Cu-942 - Enthone, Inc.
- Copper Fluoborate - Harstan, Inc.
- AC94 Bright Acid Copper - M&T Chemicals, Inc.
- Unichrome Pyrophosphate - M&T Chemicals, Inc.

Hull cell tests were used to screen the five non-cyanide copper plating systems. Bright range and throwing power were determined. Enthone's Cu-942 showed the greatest bright range and excellent throwing power. Lea-Ronal's Cu-Pure and M&T's AC-94 has a bright range and throwing power similar to the cyanide-type control; however, M&T's AC-94 had relatively high cost and maintenance requirements. Based on the Hull cell test results, the two best systems, Lea-Ronal's Cu-Pure and Enthone's Cu-942, were selected for further testing.

The selected systems were tested at their optimum current density, as determined by the Hull cell tests, in 2.5 l (0.66 gal) baths. These tests (Table 6) showed that Enthone's Cu-942 is superior to the other baths tested, including the cyanide-type control. Cu-942 gave a smooth and bright deposit and no edge burning. No gassing or foaming of the bath was observed. Neither the cyanide control nor the other non-cyanide systems matched this performance. The plating rate of Cu-942 was 1.5 times that of the cyanide control. In addition, Cu-942 showed better protection than the other systems against decarburization of steel subjected to heat treatment (829° C/1525° F for 10 min).

Final characterization testing of Cu-942 (Table 7) showed that the adhesion and solderability of the deposit are excellent. No hydrogen embrittlement was evident in notched tensile tests of the Cu-942 plated specimens. In order to substitute a non-cyanide copper plating system for a cyanide copper plating system, plating tanks must be lined with PVC or similar material to make them acid-resistant. Other special equipment is not required. Use of the cyanide waste treatment system is no longer necessary.

Alternatives to Hexavalent Chromium Plating

Chromium is extremely toxic in its hexavalent form. Hexavalent chromium in spent electroplating baths must be reduced to the trivalent form, which is much less toxic, prior to precipitation as insoluble chromium hydroxide

TABLE 4. POWDER COATINGS - SCREENING EVALUATION

RESIN	SUBSTRATE	SURFACE APPEARANCE	GLOSS	COATING ANCHORAGE	ANCHORAGE (WET TAPE)	FLEXIBILITY	IMPACT RESISTANCE	LUBE OIL RESISTANCE	RESISTANCE TO HEAT
EPOXY (POWDER SPRAY)	ALUMINUM	GOOD	96	GOOD	GOOD	PASS	PASS*	SOME DISCOLORATION	SOME DISCOLORATION
	STEEL	GOOD	93	GOOD	GOOD	PASS	PASS*	SOME DISCOLORATION	SOME DISCOLORATION
POLYESTER (POWDER SPRAY)	ALUMINUM	GOOD	79	GOOD	LIFTED IN SPOTS	FAIL-FILM CRACKING	FAIL**	SLIGHT DISCOLORATION	V. SLIGHT DISCOLORATION
	STEEL	GOOD	80	GOOD	GOOD	FAIL-FILM CRACKING	FAIL**	SOME DISCOLORATION	V. SLIGHT DISCOLORATION
NYLON (POWDER SPRAY)	ALUMINUM	GOOD	68	GOOD	GOOD	PASS	PASS*	SLIGHT DISCOLORATION	SLIGHT DISCOLORATION
	STEEL	GOOD	69	GOOD	GOOD	PASS	PASS*	SLIGHT DISCOLORATION	SLIGHT DISCOLORATION
NYLON (FLUIDIZED BED)	ALUMINUM	GOOD	68	GOOD	GOOD	PASS	PASS*	SLIGHT DISCOLORATION	DISCOLORED
	STEEL	GOOD	66	GOOD	GOOD	PASS	PASS*	SLIGHT DISCOLORATION	DISCOLORED

*7.2 JOULES (64 IN-LB)
**2.3 JOULES (20 IN-LB)

for waste disposal. Use of a trivalent chromium electroplating bath could eliminate this costly waste treatment step. In addition, the toxic spray generated during bath operation could be eliminated. A trivalent chromium plating process developed for decorative chromium plating is available from Harshaw Chemical Company.

This process, called Trichrome, was evaluated in comparison with a standard hexavalent chromium plating process (Table 8). Test panels were plated with 25.4 μm (1.0 mil) semi-bright nickel, 10.2 μm (0.4 mil) bright nickel, and 0.25 μm (0.01 mil) chrome. Appearance of the Trichrome was much brighter than the hexavalent chromium plate. The adhesion of both plates

TABLE 5. FINAL CHARACTERIZATION TESTS: REPLACEMENT COATINGS FOR ORGANIC SOLVENT PAINTS

COATING SYSTEM	SURFACE APPEARANCE	GLOSS	LOSS OF GLOSS	COATING ANCHORAGE	ANCHORAGE (WET TAPE)	FLEXIBILITY	IMPACT RESISTANCE	LUBE OIL RESISTANCE	RESISTANCE TO HEAT	RESISTANCE TO FLUIDS			HYDROLYTIC STABILITY
										JP 5	HF 5606	SKYDROL 500	
CONTROL EPOXY PRIMER POLYURETHANE TOPCOAT	VERY SLIGHT MOTTLING	89	1 UNIT	GOOD	GOOD	PASS	PASS*	SLIGHT DISCOLORATION	VERY SLIGHT DISCOLORATION	NO EFFECT	SLIGHT BLISTERING	FILM SOFTENED – LOSS OF ADHESION	NO FILM SOFTENING OR LOSS OF ADHESION, SLIGHT DISCOLORATION
EPOXY PRIMER AQUATHANE II TOPCOAT	SLIGHT MOTTLING	54	7 UNITS	GOOD	GOOD	PASS	PASS*	DISCOLORED	DISCOLORED	NO FILM DEFECTS, SLIGHT DISCOLORATION	NO FILM DEFECTS, SLIGHT DISCOLORATION	FILM SOFTENED – LOSS OF ADHESION	FILM SOFTENING, SOME LOSS OF ADHESION, DISCOLORATION
AQUALURE 631 L 128 PRIMER AQUALURE 634 W 804 TOPCOAT	GOOD	88	10 UNITS	GOOD	GOOD	PASS	PASS*	SLIGHT DISCOLORATION	VERY SLIGHT DISCOLORATION	NO FILM DEFECTS, SLIGHT DISCOLORATION	NO FILM DEFECTS, SLIGHT DISCOLORATION	FILM SOFTENED – LOSS OF ADHESION	FILM SOFTENING, DISCOLORATION
EPOXY POWDER SPRAY	GOOD	94	–	GOOD	GOOD	PASS	PASS*	SOME DISCOLORATION	SOME DISCOLORATION	NO EFFECT	NO EFFECT	FILM SOFTENED – COMPLETE LOSS OF ADHESION	BLISTERING; LOSS OF ADHESION; SOME DISCOLORATION
NYLON POWDER SPRAY	GOOD	68	–	GOOD	GOOD	PASS	PASS*	SLIGHT DISCOLORATION	SLIGHT DISCOLORATION	NO EFFECT	NO EFFECT	NO EFFECT	NO FILM DEFECTS, SLIGHT DISCOLORATION
NYLON FLUIZIDED BED	GOOD	67	–	GOOD	GOOD	PASS	PASS*	SLIGHT DISCOLORATION	DISCOLORED	NO EFFECT	NO EFFECT	NO EFFECT	NO FILM DEFECTS, SLIGHT DISCOLORATION

*7.2 JOULES (64 IN-LB)

TABLE 6. NON-CYANIDE COPPER PLATING — SCREENING TESTS

	HULL CELL TESTS		2.5 LITER (0.66 GAL) SOLUTION TESTS						
SYSTEM	BRIGHT RANGE, A/M^2(A/SF)	THROWING POWER	CURRENT DENSITY, A/M^2(A/SF)*	SURFACE CONDITION	EDGES	COMMENTS	PLATING RATE, μM/MIN (MIL/MIN)	RMS VALUE	HEAT TREAT EVALUATION
MACDERMID ROCHELTEX (CYANIDE TYPE CONTROL)	11-387 (1-36)	GOOD	270 (25)	SMOOTH	SLIGHT BURNING	EXCESSIVE GASSING	0.495 (0.020)	55-100	SOME DECARB
LEA-RONAL CU-PURE	11-324 (1-30)	GOOD	390 (36)	SMOOTH	SOME BURNING	SOME FOAMING	0.406 (0.016)	60-125	MINUTE DECARB
ENTHONE CU-942	11-1290 (1-120)	EXCELLENT	780 (72)	SMOOTH & BRIGHT	NO BURNING	NO GASSING OR FOAMING	0.813 (0.032)	45-55	NO DECARB

*OPTIMUM CURRENT DENSITY AS DETERMINED BY HULL CELL TESTS

TABLE 7. ENTHONE-ENTHOBRITE CU-942 NON-CYANIDE COPPER PLATING FINAL CHARACTERIZATION TESTS

PROPERTY	PROCEDURE	RESULTS
THICKNESS	PERMASCOPE	28-33 μM @ 0.813 μM/MIN (1.1-1.3 MILS @ 0.032 MILS/MIN)
ADHESION	SHEET BEND	EXCELLENT*
DECARB PROTECTION	METALLOGRAPHIC EXAMINATION	NO DECARB
SOLDERABILITY	SOLDER 232°C (450°F) – SHEET BEND	EXCELLENT*
HYDROGEN EMBRITTLEMENT	75% UNTS/200 HR	PASS

*COPPER PLATE IMMEDIATELY FOLLOWING NICKEL STRIKE

was good. Corrosion resistance was determined by subjecting panels to 5% salt spray solution until failure. Although the hexavalent chromium showed more consistent results, the Trichrome averaged three times longer exposure until failure. This indicates that the trivalent process can provide longer corrosion protection for the substrate. The scatter in the data for the Trichrome panels indicates that additional work is needed to provide consistently good results with this process. However, these results do show that trivalent chromium is a viable alternative to hexavalent chromium plating. Sustained-load tests were also performed to determine the presence of hydrogen embrittlement. Notched tensile specimens (4340 steel) were heat treated to 1790-1930 MPa (260-280 ksi), plated and baked for three hours for embrittlement relief. The Trichrome-plated specimens exceeded the 200-hour exposure at 75% of ultimate notched tensile strength with no failure. The hexavalent chromium specimens, on the other hand, all failed in less than seven hours.* These failures may also be due to differences in the nickel baths used.

Conversion of existing hexavalent chromium plating operations requires that the lead-lined tanks be lined with rigid plastic sheet. Lead anodes are replaced with carbon anodes, which do not deteriorate as the lead anodes do. No other major changes are required. The chromium reduction step can be eliminated from the waste treatment process.

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*Normally, chrome plating on high-strength steel is baked for 23 hrs to provide complete hydrogen embrittlement relief.

TABLE 8. TRIVALENT CHROMIUM PLATING: PERFORMANCE EVALUATION

PROPERTY	TRICHROME*	HEXAVALENT CHROMIUM*
APPEARANCE	SMOOTH AND VERY BRIGHT	SMOOTH AND BRIGHT
ADHESION (BEND TEST)	GOOD	GOOD
CORROSION RESISTANCE (5% SALT SPRAY)	48 TO 744 HRS** 288 HRS AVG	96 HRS***
HYDROGEN EMBRITTLEMENT	PASS 200 HRS @ 75% UNTS	FAIL @ 4.9 HRS @ 75% UNTS

*DECORATIVE CHROMIUM – 25.4 μM (1.0 MIL) SEMI-BRIGHT NICKEL
10.2 μM (0.4 MIL) BRIGHT NICKEL
0.25 μM (0.01 MIL) CHROME (TRIVALENT OR HEXAVALENT)

**FOUR PANELS TESTED

***EACH OF THE FOUR PANELS FAILED AT 96 HRS

TABLE 9. CADMIUM PLATING — HULL CELL TESTS

PLATING SYSTEM	BRIGHT RANGE A/M^2(A/SF)	DEPOSITION RATE, μM/MIN (MILS/MIN) AT 430A/M^2 (40 A/SF)	PLATE THICKNESS* μM (MILS)	APPEARANCE
ENTHOBRITE CYANIDE CADMIUM	54-430 (5-40)	0.76 (0.03)	1.52 (0.06)	BURNT DEPOSIT AT HIGHER CURRENT DENSITIES
KADIZID	54-1075 (5-100)	0.64 (0.025)	1.27 (0.05)	BRIGHT
CAD-AL (49°C)	54-540 (5-50)	0.25 (0.01)	0.51 (0.02)	SEMI-BRIGHT
CAD-935	22-1190 (2-110)	0.51 (0.02)	1.02 (0.04)	DISCOLORED

*HULL CELL TEST RUN AT 3 AMPS FOR 2 MINUTES

Alternatives to Cyanide Cadmium Plating

Several alternatives to cyanide cadmium plating are available, both as solutions to the use of cyanide and to the use of cadmium, which are both highly toxic. Costly waste treatment is required to minimize environmental contamination. Non-cyanide cadmium plating, mechanical plating, spray-and-bake aluminum coatings, and ion vapor deposition (IVD) of aluminum have been evaluated as potential alternatives to cyanide cadmium electroplating.

Three non-cyanide cadmium plating systems were evaluated. These systems were Lea-Ronal's Kadizid, Lea-Ronal's Cad-Al, and Enthone's Enthobrite CAD-935. Deposition rate and brightness of these systems were determined by Hull cell tests (Table 9). Kadizid showed the greatest bright range and thickest deposits in these tests. The appearance of the Kadizid plate was also better

TABLE 10. KADIZID NON-CYANIDE CADMIUM PLATING/THROWING POWER — BENT CATHODE TEST

CURRENT DENSITY, A/M² (A/SF)	TIME, MIN	PLATE THICKNESS, μM (MILS)			COMMENTS
		AREA 1*	AREA 2*	AREA 3*	
86 (8)	15	1.02 (0.04)	1.02 (0.04)	2.03 (0.08)	EXCELLENT
194 (18)	15	3.05 (0.12)	3.05 (0.12)	8.38 (0.33)	EXCELLENT
302 (28)	15	7.11 (0.28)	4.32 (0.17)	12.7 (0.50)	EXCELLENT
410 (38)	15	9.14 (0.36)	9.14 (0.36)	14.5 (0.57)	PITTING IN AREA 2
518 (48)	15	13.5 (0.53)	12.4 (0.49)	19.1 (0.75)	PITTING OVER ENTIRE SURFACE, STREAKING IN AREA 3

*WHERE

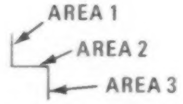

TABLE 11. EVALUATION OF MECHANICALLY PLATED COATINGS

PROPERTY	MECHANICALLY PLATED		CYANIDE CADMIUM ELECTROPLATE (WITH CHROMATE CONVERSION COATING)
	CADMIUM (WITH CHROMATE CONVERSION COATING)	TIN CADMIUM	
APPEARANCE	SCRATCHED	SCRATCHED	SMOOTH
ADHESION	PASS	PASS	PASS
CORROSION RESISTANCE, HRS TO FAILURE IN 5% SALT SPRAY			
SUBSTRATE – D6AC	2664+	516	2118+
4340	1800+	558	2514
HYDROGEN EMBRITTLEMENT 200 HRS @ 75% UNTS (260 KSI)	PASS	–	PASS (23 HR BAKE)

than that of the other non-cyanide systems, as well as that of the cyanide system used as a control.

Kadizid was selected for further testing. Throwing power, as determined by the bent cathode test (Table 10), is excellent. A smooth bright finish was obtained when Kadizid was used to plate an etched panel, showing the good leveling power of Kadizid. The adhesion of the Kadizid plate is excellent. Corrosion tests were run on panels plated to 15.2 to 22.9 um (0.6 to 0.9 mils) with Kadizid and chromate conversion coated. These panels passed the standard 168-hr salt spray test. Hydrogen embrittlement was not evident in 1790-1930 MPa (260-280 ksi) high-strength steel plated with Kadizid and baked for 23 hrs at 191° C (375° F) for embrittlement relief. This strength level was used for test purposes only; normally, cadmium electrodeposition is restricted to 1655 MPa (240 ksi) or less. These specimens exceeded 200 hrs at 75% ultimate notched tensile strength (UNTS) without failure.

The advantage of the non-cyanide type electroplating system is that a direct substitution can be made for current cyanide-type systems with no loss of quality. Equipment must be lined with PVC or other acid-resistant material; no other equipment changes are required. In addition, waste treatment of cyanides will not be required.

Mechanically plated cadmium and tin-cadmium were also evaluated. The 3M Company's Transiflo process was

TABLE 12. SPRAY AND BAKE ALUMINUM COATINGS

PROPERTY	TIODIZE ALUMAZITE Z EPOXY PRIMER	HI-SHEAR HI-KOTE 3 NO PRIMER	HI-SHEAR HI-KOTE 3 EPOXY PRIMER
ADHESION – BEND TEST	NO LIFTING OR PEELING	NO LIFTING OR PEELING	NO LIFTING OR PEELING
CORROSION – SALT SPRAY	700 HR TO RED RUST*	300 HR TO RED RUST**	200 HR TO RED RUST**
FLUID RESISTANCE (R.T.)			
– SKYDROL 500	HEAVY WHITE PPT @ 650 HR***	WHITE PPT @ 96 HR GOOD ADHESION @ 4000 HR	–
– 5606 HYDRAULIC FLUID	NO EFFECT @ 4000 HR	NO EFFECT @ 4000 HR	
– DIESTER OIL	NO EFFECT @ 4000 HR	NO EFFECT @ 4000 HR	
THICKNESS	5.1 – 12.7 μm 0.2 – 0.5 mils	10.2 – 12.7 μm 0.4 – 0.5 mils	–
HYDROGEN EMBRITTLEMENT	PASS 200 HRS @ 75% UNTS (3 SPECIMENS)	—	–

*AVERAGE OF 2 PANELS
**AVERAGE OF 4 PANELS
***LOSS OF ADHESION OCCURRED PRIOR TO 4000 HRS

TABLE 13. CYANIDE CADMIUM REPLACEMENT COATINGS — ADVANTAGES AND DISADVANTAGES

CYANIDE CADMIUM	NON-CYANIDE CADMIUM	MECHANICAL PLATING	SPRAY-AND-BAKE ALUMINUM	IVD ALUMINUM
		ADVANTAGES		
• READILY AVAILABLE	• REDUCES WASTE TREATMENT REQ'D	• ELIMINATES CYANIDES	• ELIMINATES CYANIDES	• ELIMINATES CYANIDES
• TECHNIQUES WELL-ESTABLISHED	• ELIMINATES CYANIDES	• ELIMINATES HYDROGEN EMBRITTLEMENT	• ELIMINATES CADMIUM	• ELIMINATES CADMIUM
• PROVEN SYSTEM	• CONVERSION COSTS LOW		• REDUCES WASTE TREATMENT REQ'D	• ELIMINATES WASTE TREATMENT REQ'D
			• ELIMINATES HYDROGEN EMBRITTLEMENT	• ELIMINATES HYDROGEN EMBRITTLEMENT
			• USES CONVENTIONAL SPRAY EQUIPMENT	• USE TO 510° C (950° F) (CD LIMITED TO 232° C-450° F)
			• CAN BE FORMULATED FOR MAX. PERFORMANCE	
		DISADVANTAGES		
• USES TOXIC CHEMICALS	• HIGHER MAKE-UP COST	• REQUIRES NEW EQUIPMENT	• ORGANIC SOLVENT COLLECTION SYSTEM REQ'D	• REQUIRES NEW EQUIPMENT
• REQUIRES COSTLY WASTE TREATMENT		• PART SIZE LIMITED		

used for application of these coatings. Bend tests showed that the adhesion of the mechanical plate is satisfactory. The corrosion resistance of the mechanically plated cadmium with a chromate conversion coating is approximately the same as that of the cyanide cadmium electroplate with chromate conversion coating (Table 11). Tin cadmium was not chromate conversion-coated and showed a much lower corrosion resistance. All panels were tested in 5% salt spray to failure in order to assess their relative corrosion resistance. High-strength steel [1790 - 1930 MPa (260 - 280 ksi) and 2070 MPa (300 ksi)] that has been mechanically plated is free from hydrogen embrittlement.

New equipment must be obtained for mechanical plating. Presently available mechanical plating equipment limits the largest part dimension to 20 cm (8 in.) and the part weight to less than 230 g (0.5 lb).

Two spray-and-bake aluminum coatings, Alumazite Z (Tiodize Company) and Hi Kote 3 (Hi Shear Corporation), were evaluated. These coatings are

TABLE 14. CYANIDE CADMIUM REPLACEMENT COATINGS

SYSTEM	ADHESION (BEND TEST)	CORROSION RESISTANCE HRS TO FAILURE***			HYDROGEN EMBRITTLEMENT
		4130	4340	D6AC	
CYANIDE CADMIUM ELECTROPLATE*	GOOD	576	2514	2118+	PASS
NON CYANIDE CADMIUM ELECTROPLATE* (KADIZID)	EXCELLENT	–	PASS 168**	–	PASS
MECHANICAL CADMIUM PLATING*	GOOD	–	1800+	2664+	PASS
SPRAY & BAKE ALUMINUM (ALUMAZITE Z)	EXCELLENT	700	–	–	PASS
IVD ALUMINUM	EXCELLENT	1752	–	–	–

*CHROMATE CONVERSION COATING APPLIED TO PLATED PANEL
**NOT TESTED TO FAILURE
***AVERAGE OF 4 PANELS

aluminum-filled resins that are sprayed onto the substrate. Both coatings exhibit excellent adhesion (Table 12) with or without epoxy primer (conforming to MIL-P-2337). The corrosion resistance of these coatings is also good. The Alumazite Z coating requires the use of an epoxy primer to provide adequate corrosion protection (over 168 hrs in 5% salt spray). Without the primer, panels coated with Alumazite Z failed within 96 hrs in 5% salt spray. use of the epoxy primer increased the corrosion protection of Alumazite Z to over 700 hrs in salt spray. The Hi Kote 3 coating will withstand 300 hrs in salt spray without primer. With epoxy primer, corrosion protection was slightly decreased (Table 12). Both of these coatings exhibit excellent resistance to hydraulic fluid, diester oil, and Skydrol 500 (Table 12). There is no evidence of hydrogen embrittlement in coated specimens of high-strength steel [1790-1930 MPa (260-280 ksi)].

Application of these coatings is accomplished with conventional spray equipment. Because cyanide and cadmium are not used, waste treatment costs are minimal. An organic solvent recovery system, however, is required for pollution control. It is expected that a waterborne, spray-and-bake aluminum system may be developed in the near future. These coatings can be used in a wide variety of applications because they can be formulated for maximum performance.

Ion vapor deposition (IVD) of aluminum was evaluated for adhesion and corrosion resistance. The adhesion of IVD aluminum, as determined by the bend test, is excellent. IVD aluminum withstood an average of 1700 hours of salt spray to failure. Although special equipment is required for application of this coating, waste treatment is not required. Part size, however, is a limitation; the maximum part size that can be coated at this time is 2.1 × 3.7 m (7×12 ft), which is sufficient for most applications. The temperature limitation for IVD aluminum is 510° C (950° F) compared to 232° C (450° F) for cadmium.

None of the coating types evaluated can be considered optimum for replacement of cyanide cadmium plating in all applications. The advantages and disadvantages of each coating type are summarized in Table 13. These must be weighed with the relative performance of the coatings (Table 14) to determine the best coating for a specific application in terms of cost, performance and waste treatment requirements, and environmental compatibility.

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Evaporative Recovery in Electroplating

Howard S. Hartley*

This presentation will review the role of evaporation in plating waste recovery, the economics of recovery, and it will examine the types of evaporators available for recovery systems.

Not too long ago, the cost determination for plating parts was straight forward and consisted of figuring the cost of chemicals, utilities and labor. The cost of liquid wastes was simply the cost for plant water. Today, plating cost determinations are more complex because the cost of waste treatment has become a significant part of the plating cost. To sharpen their competitive situation, platers must be familiar with the treatment technologies available for plating wastes.

In most instances, treatment of an industrial waste is an expense which adds to the usual cost of production. Sometimes, however, it is possible to recover valuable products or by-products from individual waste sources to help defray the total cost of waste treatment. Plating happens to be one of those industrial operations where there exists the opportunity for economic waste recovery. Furthermore, this recovery can be accomplished by in-process recycle to the front end of the process; a most desirable form of recovery.

Block diagram, Fig. 1, shows how an evaporative recovery system can recover plating chemicals, metals, and water in a closed loop manner. Plating solution dragged out by the work is removed in a series of counter-flow rinse tanks. The first rinse tank contains the most concentrated rinse water and this is sent to a recovery system which separates it via evaporation into original components; plating solution and rinse water. The plating solution is returned to the plating tank and the distilled water is recycled to the last rinse tank.

Fig. 2 allows a more detailed look at the operation of an evaporative recovery system. This is a typical single effect system. Contaminated rinse water from the first rinse tank overflows to an intermediate tank which is called a feed tank. From here the rinse water is drawn into the evaporator which operates under vacuum conditions. In the evaporator the rinse water solution passes through the tubes of a shell and tube heat exchanger commonly called a reboiler. Steam is introduced in the shell side of the reboiler. Because the solution is at a lower temperature than the steam, the steam condenses and transfers its heat energy through the wall of the reboiler tubes to the solution. This action causes the plating solution to boil. Water is evaporated and passes through a de-entrainment device to remove entrained droplets of plating solution. The distilled water vapor then enters the condenser which is another shell and tube heat exchanger. Cooling water at a lower temperature than the water vapor removes heat and causes it to condense. The distilled water is then returned to the final rinse tank. The concentrated plating solution remaining in the evaporator is returned to the plating tank. No chemicals are added or discharged to the sewer. This concept is called closed-loop recovery because it virtually closes off any plating solution discharge.

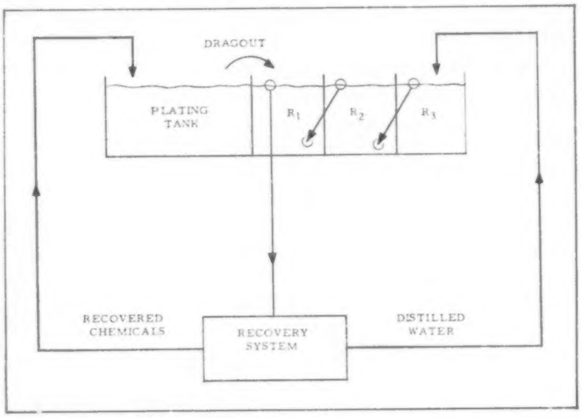

Fig. 1—Closed-loop recovery.

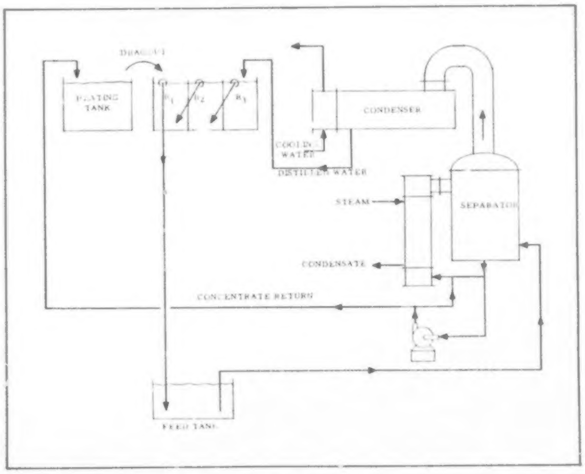

Fig. 2—Single-effect evaporator.

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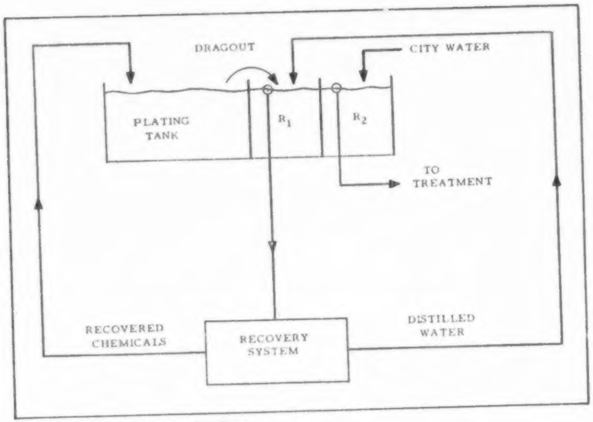

Fig. 3—Open-loop rinsing.

The key to evaporative closed-loop recovery is multiple counterflow rinse tanks, which help concentrate the chemicals in rinse water and drastically reduce the required rinse water flow rate. For example, the amount of rinse water required for 1, 2 or 3 counterflowed rinse tanks in order to achieve the same concentration level in the final rinse, 7300 gal/hr of water are needed for one rinse; with two rinses this drops to 85.5 gal/hr and with three counterflowed rinses only 19.5 gal/hr of water are required. The optimum number of counterflowed rinse tanks is usually 3 to 5, but there are plating lines with only two rinse tanks and it may be impractical to add more. In this case, economic recovery can still be achieved by recovering the plating chemicals from only the first rinse tank. This is shown by Fig. 3 and is referred to as open-loop rinsing. Using this approach, sometimes more than 90% of the dragout can be recovered from the first rinse tank. The remaining 10% entering the second rinse tank is sent to chemical treatment or a demineralizer can be used to recover the water.

Evaporative recovery can be applied to practically all types of plating solutions. Systems have been furnished for cyanide baths for zinc, cadmium, copper, silver and brass; various proprietary chromic acid baths; nickel baths; fluoborate solutions for tin, lead-tin and lead-tin-copper; and zinc chloride solutions.

The possible build-up of impurities in the bath caused by recycling recovered dragout is a legitimate concern. Proven techniques are available, however, to purge excess impurities from the various plating baths. For chrome baths, the chief impurities are tramp metals and excess trivalent chromium. These are removed by installing a cation exchanger in the contaminated rinse water stream before it enters the evaporator. For nickel plating, purification is achieved in the normal circulation of solution through an activated carbon filter. In cyanide baths, carbonates, created by the decomposition of sodium cyanide, are the principle impurities, and these can be removed by either freezing them out or by chemical precipitation.

Solution	\$/Gal. Value	\$/Gal. + Treatment =	\$/Gal. Total
Cad. Cyanide	1.00	3.00	4.00
Chromic Acid	2.00	1.00	3.00
Nickel	3.50	0.50	4.00

Fig. 4—Recovery & potential.

Generally, the main reason for choosing an evaporative recovery system is that it provides an economic solution to a pollution problem. Several years ago recovery systems were sold only on the basis that the value of recovered plating solution would pay for the system in 3 years or less. Today, the new environmental laws have added other economic considerations: the cost of chemical treatment, heavy metal removal and sludge disposal. Now, some of the least expensive plating solutions, such as the metal cyanides, offer very attractive economics because their treatment costs are relatively expensive. Fig. 4 shows plating solution value in terms of \$/gal and their estimated chemical treatment cost. Notice that the inexpensive cadmium cyanide solution has the same total economic justification for recovery as the relatively expensive nickel solutions. Thus, a cadmium barrel plating operation which has a dragout rate of 5 gph and operates 4000 hours/yr has a gross savings potential of \$80,000/year. Of course the operating expenses of the recovery system must be deducted from the savings and these depend on the evaporative capacity of the system and the type of evaporator.

The evaporative capacity of a recovery system is expressed as gallons/hour, gph, and equals the amount of rinse water required to satisfy the rinsing requirements dictated by the number of available counterflowed rinse tanks, the dragout rate and the concentration of plating solution. Once the evaporative capacity has been determined, the selection of the type of evaporative recovery system can be considered. There are basically three types of evaporators available for plating waste recovery systems: single-effect, multiple-effect and vapor recompression.

The single-effect evaporator has been the most popular type for recovery systems for two main reasons: 1) its low capital cost and 2) its simple operation. At least four types of single-effect evaporators have been used for plating waste recovery systems:

a. atmospheric tower
b. submerged tube
c. rising-film thermosyphon
d. flash evaporator

Neglecting heat losses to the surroundings, all single effect vacuum evaporators require approximately 1.07 lbs. of steam to evaporate 1.0 lb. of water. Therefore, their operating costs are nearly the same.

The atmospheric tower evaporator requires more steam because it must heat large quantities of air in addition to supplying the energy to evaporate the water. Fig. 5 shows a schematic of an atmospheric tower. The contaminated rinse water is pumped through a steam heated heat exchanger at a high flow rate because the

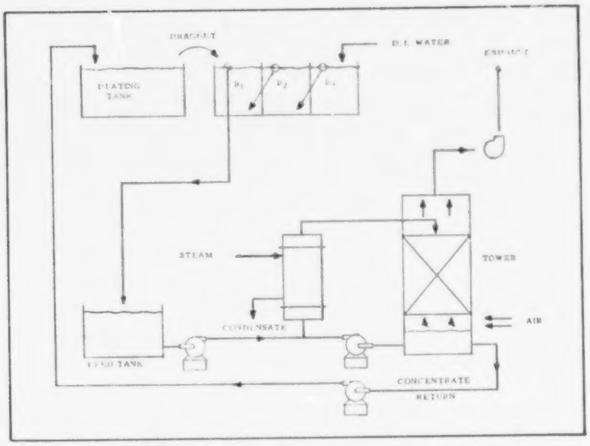
DRAGOUT
D.I. WATER
EXHAUST
PLATING TANK
R_1
R_2
R_3
STEAM
TOWER
AIR
CONDENSATE
FEED TANK
CONCENTRATE RETURN

Fig. 5—Atmospheric tower.

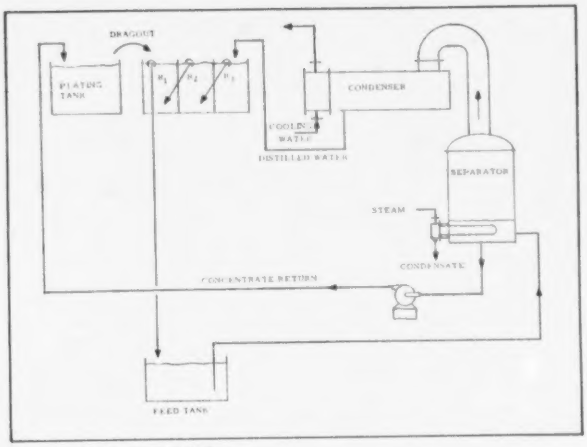
DRAGOUT
PLATING TANK
R_1
R_2
R_3
CONDENSER
COOLING WATER
DISTILLED WATER
SEPARATOR
STEAM
CONDENSATE
CONCENTRATE RETURN
FEED TANK

Fig. 6—Submerged tube.

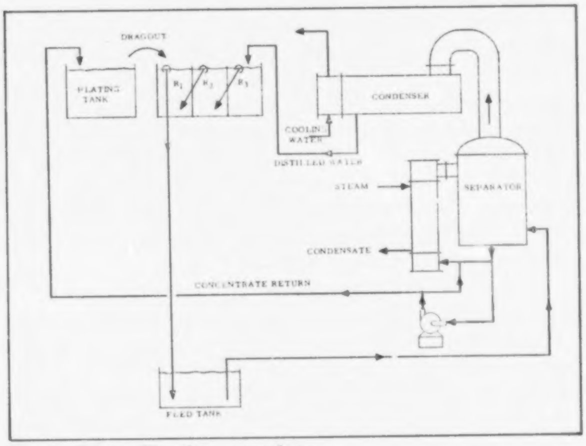
DRAGOUT
PLATING TANK
R_1
R_2
R_3
CONDENSER
COOLING WATER
DISTILLED WATER
STEAM
SEPARATOR
CONDENSATE
CONCENTRATE RETURN
FEED TANK

Fig. 7—Rising film thermosyphon.

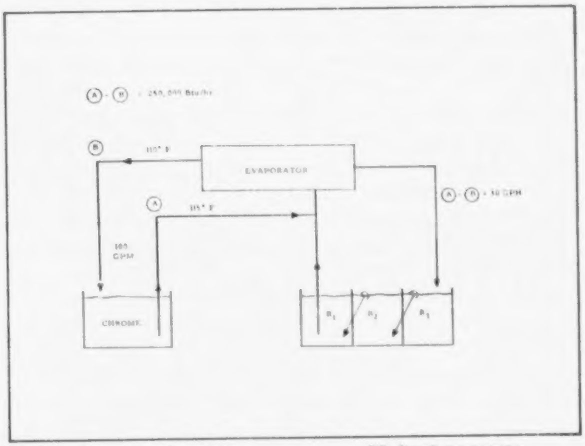
Ⓐ - Ⓑ = 250,000 Btu/hr
Ⓑ
110° F
EVAPORATOR
Ⓐ
115° F
Ⓐ - Ⓑ = 30 GPH
100 GPM
CHROME
R_1
R_2
R_3

Fig. 8—Chrome closed-loop recovery with heat recovery.

heat required to evaporate the water and heat up the air must be supplied by this stream in the form of sensible heat. The heated rinse water stream enters the top of the tower, trickles over and down the tower's internal packing and contacts the air flow which is traveling in a counterflow direction up the column. Water is evaporated by humidification of the air stream. Its main advantages are: it can double as a fume scrubber, and it does not need cooling water. It has several disadvantages: 1) its application is limited to plating solutions unaffected by the oxidizing nature of air; 2) it requires 20 - 25% more heat energy than other single effect evaporators; 3) it does not recover distilled water for rinsing.

The submerged tube evaporator uses a horizontal heat exchanger for the reboiler as shown by Fig. 6. Here the solution is on the outside of the tubes and steam is on the inside. This design offers a compact system, but it may be more difficult to clean the exterior of tubes versus the interior if fouling of the tubes occurs.

The rising film thermosyphon evaporator is shown schematically by Fig. 7. It usually has a vertical shell and tube heat exchanger called the reboiler with the solution on the inside of the tubes and the condensing steam on the outside of the tubes. The unit can operate with natural circulation or forced circulation supplied by pump.

The flash evaporator is basically a rising film evaporator, but it can operate at a temperature below that of some plating baths. This permits the evaporator to recover waste electrolytic heat generated in the plating bath by recirculating plating solution through the evaporator and "flash cooling" it to a lower temperature. The excess heat is "flashed-off" as water vapor and condensed as distilled water. Thus, the steam required to achieve the desired evaporation rate (rinse water flow rate) can be reduced accordingly. In Fig. 8 for example, approximately 250,000 Btu/hr of waste electrolytic heat are converted into 30 gph of distilled water. This saves almost 270 lbs/hour of steam. Evaporative recovery systems have been designed to recover as much as 5,000,000 Btu/hr of waste electrolytic heat from chromic acid plating baths. In some cases, cooling coils in the plating tank have been eliminated and the recovery system has been used to control the bath temperature.

The majority of the single effect evaporator's operating cost is for steam energy. Steam at $3.50/1000 lbs translates to $0.30/gallon of distilled water produced. The quantity of cooling water required to condense the distilled water varies with the allowable temperature rise of cooling water. For a 40° F temperature rise, 25 gallons of cooling water are required for each gallon of distilled water. The cooling water flow is high in comparison to the distilled water flow because each lb of condensing distilled water has a latent heat of vaporization of 1000 Btu while each lb of cooling water can take away only 40 Btu at a 40° F temperature rise. The existing cooling water contains practically all of the energy which was consumed by the recovery system as steam. This warm cooling water is not contaminated and can be beneficially used for other rinsing operations. Warm water does a more effective rinsing job than cold water, especially for alkaline cleaner rinses. If there is not a need for the total flow of cooling water, then the use of cooling tower to recirculate the cooling water should be examined from an economic viewpoint. Other cooling water consumers such as bath cooling coils, rectifiers and air compressors could also be included in the cooling tower system.

Recovery systems also require electrical power to operate pumps and control panels. This power requirement is generally small in comparison to the steam energy. In addition to the steam, cooling water and electrical power, most evaporative recovery systems need a couple cfm of compressed air to operate pneumatic controls.

The capital cost of a single effect evaporator is dependent upon two main factors: 1) its evaporative capacity and 2) its application which dictates the materials of construction. A recovery system designed for cyanide-type plating solutions needs only carbon steel components to withstand the environment. Chromic acid plating solutions are extremely corrosive and necessitate the use of expensive materials of construction such as tantalum for the reboiler heat exchanger. The cost of an evaporative recovery system having an evaporative capacity of 60 gallons/hr (gph) would be less than a system with an evaporative capacity of 120 or 200 gph. For these reasons it is difficult to discuss capital costs of single effect evaporators. Instead, the capital costs of all the types of evaporators discussed here will be compared on a relative scale. These will be reviewed after the other types of evaporators have been discussed.

The rising-film thermosyphon, submerged tube and flash evaporators can also be designed as multi-effect evaporators. A typical double-effect evaporator is shown by Fig. 9. As can be seen, it resembles two single-effect evaporators connected in series except there is only one condenser. Steam is introduced at the first effect and as with the single-effect evaporator, approximately 1 lb of water is evaporated per lb of steam. The 1 lb of water evaporated in the first-effect, however, becomes the steam supply for the second effect. This one lb evaporates about 1 lb of water in the second effect. Thus, in a double-effect evaporative recovery system, 1 lb of steam evaporates 2 lbs of water. So the steam consumption is reduced by approximately 50% as compared to a single-effect and the cooling water consumption is also reduced by 50%.

The double-effect system requires more equipment and thus costs more than the same capacity single-effect system. A double-effect system is usually justified by comparing the steam and cooling water savings against the extra capital cost. Generally, a double-effect evaporative recovery system is used for larger evaporative capacities because steam savings are insignificant for small systems.

There are other factors besides energy savings which should be weighed when considering a double-effect system. The first effect of the evaporator must operate at a higher temperature in order for its evaporated water to be the heat source for the second effect. This higher temperature may be detrimental to heat-sensitive solutions such as some of the cyanide baths. Another consideration is the skill and experience of operators who will be running the recovery system. The operation of a double-effect system is more complex than a single effect.

Evaporators can be designed with more than two effects, but generally, for the electroplating industry, the required evaporative capacity is not large enough to justify more than two effects.

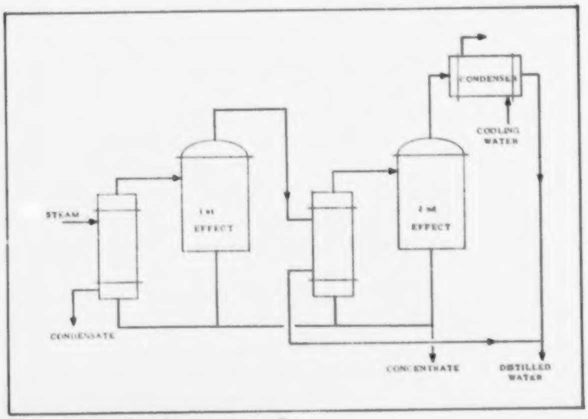

Fig. 9—Double effect evaporator.

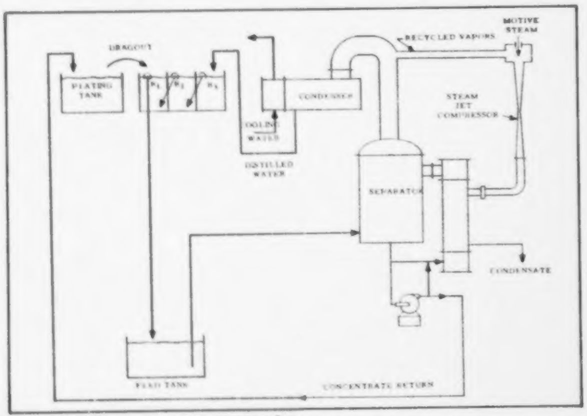

Fig. 10—Thermal recompression

So far this paper has reviewed single and multiple effect evaporators. The last type to be discussed is vapor recompression. There are two types of vapor recompression evaporators: thermal and mechanical.

A typical thermal vapor recompression evaporator is shown in Fig. 10. This one consists of a single effect evaporator, although it can also be used with multiple effect evaporators, and a thermocompressor which is a steam jet. The purpose of the thermocompressor is to reduce the steam requirement and operating cost of the evaporator. Part of the water evaporated enters the thermocompressor which compresses it with motive steam to a slightly higher temperature and pressure. Thus, this part of the evaporated water becomes the steam to evaporate additional water. The steam economy of a single-effect evaporator with a thermocompressor is about equal to a double-effect evaporator. A limitation of this system is the high pressure steam requirement, 100 psi or higher, for the thermocompressor. Also, the water vapor entering the compressor becomes mixed with the thermocompressor's steam condensate — and complicates the recycle of distilled water. Because of this problem and the high pressure steam requirement, thermal vapor recompression has very limited appeal as a plating waste recovery system.

Mechanical vapor recompression, commonly referred to as MVR, does not have these drawbacks. A typical MVR evaporator is shown by Fig. 11. This evaporator is generally considered to be the most efficient evaporator in terms of energy consumed per lb. of water evaporated. Notice that this system does not use either steam or cooling water. It requires only electrical power to operate its motor. In the MVR system, all the water vapor leaving the evaporator enters a compressor which boosts its pressure slightly and allows it to be used as steam to evaporate additional water. The reboiler does double duty as the condenser.

Large MVR evaporators can evaporate a lb of water and consume only 30 - 40 Btu of energy. Compare this to the 1000 Btu of energy required for a single effect evaporator and it is evident that an MVR system is equivalent to a 30 effect evaporator from an energy viewpoint. When the cost differential between steam and electrical energy is applied, MVR's operating costs are equivalent of up to 15 effects. This translates to a cost of approximately $0.002/gal. of water evaporated.

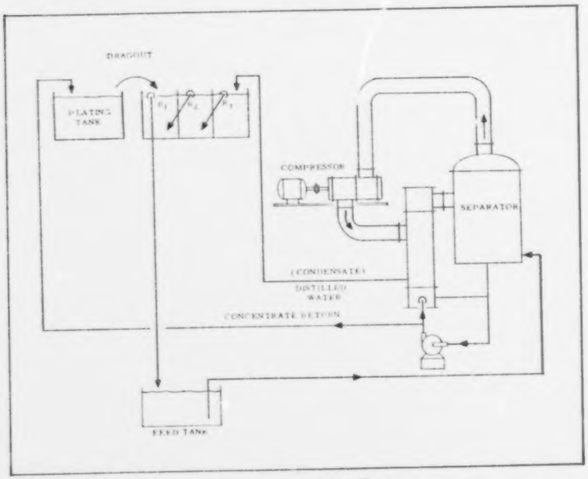

Fig. 11—Mechanical vapor recompression.

	Single Effect	Double Effect	MVR
Steam	6.35	3.50	0
Cooling Water	0.70	0.40	0
Electricity	0.15	0.15	1.25
Total $/Hr	7.20	4.05	1.25

Fig. 12—Typical operating costs, $/hr 200 GPH evaporator.

	Evaporative Capacity		
Evaporator	50 GPH	100 GPH	200 GPH
Single Effect	100	115	140
Double Effect	N. P.	145	180
MVR	N. P.	170	210

N. P. = Not Practical

Fig. 13—Relative capital costs "evaporative recovery systems."

MVR is more expensive than single and double effect evaporators; however, the cost gap narrows if a steam boiler and cooling tower must be added to serve the conventional steam heated evaporators.

MVR evaporators have been successfully used for recovery systems handling cyanide solutions. Their application has been limited to alkaline solutions because the compressors are built of cast iron and steel components. They have also been used as waste concentrators to reduce large volumes of dilute wastes prior to off-site disposal. As the cost of energy increases, demand for more corrosion-resistant compressors will grow. Either stainless steel or plated compressors would open up applications for many other plating solutions.

Now let's look at the relative capital costs and operating costs of the single-effect, double effect and MVR evaporators. Fig. 12 shows some typical hourly operating costs for steam, cooling water and electricity for a 200 gph evaporator. If the 200 gph evaporative recovery systems are operated 6000 hours/year, the single effect system's utilities would cost $42,000; the double effect system's would cost $23,700; and the MVR's would cost $7500.

As expected, a double-effect evaporator costs more than a single-effect and an MVR evaporator costs more than a double effect. How much more depends on the materials of construction and the operating conditions. Fig. 13 provides a relative cost comparison of evaporative recovery systems designed for alkaline plating solutions. The cost differential among evaporative recovery systems designed for acid-type plating solutions would be greater. Notice that a recovery system with an evaporative capacity of 200 gph costs only 40% more than a 50 gph system. A 200 gph system can be operated at a reduced capacity of 50 gph. Consider that a larger recovery system can be purchased now for a small premium and have reserve capacity for future business growth and to handle a larger dragout produced by different future parts.

In summary, when solving plating waste pollution problems, recovery and recycle should be considered when economics are feasible. Important factors to consider are the value of the metals and chemicals in the dragout, the cost of alternative chemical treatment and sludge disposal.

Evaporative recovery systems have been used for the past 25 years for various plating solutions including cyanides, chrome, nickel, fluoborates and chlorides. Field data proves that evaporative recovery systems are practical and savings are real. Optimized systems have been installed which utilize waste electrolytic heat in lieu of steam and have purification loops to prevent build-up of contaminants.

Larger evaporative capacity systems are available at a small premium, but can be operated at reduced capacities for the present and provide reserve capacity for the future. For larger recovery systems, double effect and MVR evaporators should be considered as the basis of energy savings.

Recovery is a practical conservation approach which offers the best long-range solution to both pollution abatement and conservation of scarce materials. Its use merits consideration by all platers.

Processes for Heavy Metal Removal From Plating Wastewaters

R. E. Wing*

INTRODUCTION

Effective waste treatment processes are needed to meet the stringent effluent standards that are to be set for the electroplating industry. This urgent need has encouraged researchers to develop new chemical and physical processes for meeting these standards. It will be costly to design effective treatment processes for the various rinse waters of the plating industry. Some rinses will have to be segregated for special treatments, while others can be processed by conventional treatment. The use of dragout tanks, counter flow rinsing, and other water use reduction methods is a good start; however, the use of plating baths that contain unknown proprietary chemicals does add problems to treatment design. The following discussion may suggest solutions to some of the treatment problems.

Over the last few years, numerous publications and patents have appeared describing technology effective for the treatment of plating rinse waters. Very little of this technology has gained wide acceptance for various reasons, including inadequate promotion, limited adaptability, unfavorable economics, and uncertainty of the forthcoming effluent standards.

For 6 years at NRRC, we have been developing starchbased products for heavy metal removal. Starch, a naturally occurring polymer derived from agricultural crops, is very abundant, annually renewable, and relatively inexpensive. Initially, we used a water-soluble starch xanthate to bind heavy metal cations in solution and then used a cationic polymer to yield a polyelectrolyte complex insoluble in water which contained the heavy metals (1-3). The use of a two-component system in the process and less than favorable economics prevented its broad acceptance. Therefore, we modified the process to eliminate the expensive cationic polymer by using a crosslinked, water-insoluble starch as starting material. We prepared several insoluble starch-based products containing xanthate (4-8), carboxyl (9), quaternary ammonium (10), and tertiary amine groups (10). These products have been evaluated as potential heavy metal scavengers.

Insoluble Starch Xanthate

Water-insoluble starch xanthate (4-8) (ISX) offers industry a low-cost product that removes and recovers heavy metal cations from wastewaters (Figure 1). The effectiveness of ISX for removing uncomplexed heavy metals from water can be seen in Tables 1 and 2. The data show that heavy metals are removed from concentrated solutions and dilute solutions, in most cases to concentrations below present discharge limits. From these data, ISX appears to be effective in removing metal ions at different concentration levels. If initial metal concentrations in an industrial effluent exceed 100 mg/l, it probably would not be economical to use ISX, and removal by chemical precipitation or another process could be used. In these cases, the ISX could then be used in a secondary treatment to further lower metal concentrations below discharge limits. From our studies on ISX to date, the following statements can be made:

(a) Its average capacity is 1.1 - 1.5 meq of metal ion/g ISX.

(b) It is effective over pH range of 3-11 with maximum effectiveness above pH 7.

(c) Salt concentrations of up to 10% have little influence on the effectiveness of ISX.

(d) ISX instantaneously removes metal ions from solution.

(e) Treatment is applicable to batch-type or continuous flow systems.

(f) ISX-metal sludge settles rapidly and dewaters to 30

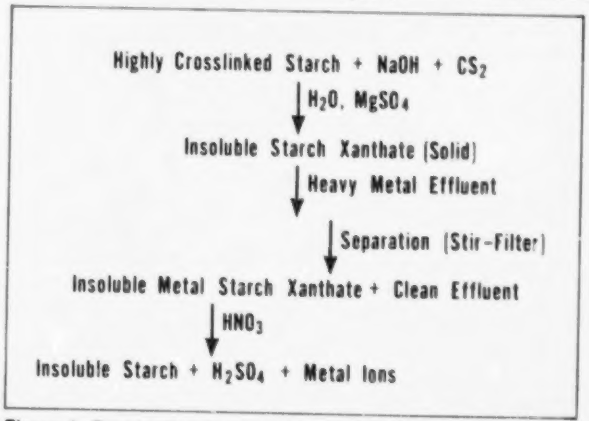
Highly Crosslinked Starch + NaOH + CS_2
H_2O, $MgSO_4$
Insoluble Starch Xanthate (Solid)
Heavy Metal Effluent
Separation (Stir-Filter)
Insoluble Metal Starch Xanthate + Clean Effluent
HNO_3
Insoluble Starch + H_2SO_4 + Metal Ions

Figure 1. Preparation and use of insoluble starch xanthate (ISX).

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- 90% solids content after filtration or centrifugation.

(g) Metals can be recovered from the ISX-metal sludge by nitric acid treatment or incineration.

(h) Preliminary cost-to-make estimate for ISX is $0.75/kg.

ISX acts as an ion-exchange material removing the heavy metal ions and replacing them with sodium and magnesium. The ISX can be added as a slurry for continuous flow operations or in the solid form for batch treatments. Recently, ISX has been shown to be effective as a precoat to a filter.

TABLE 1
REMOVAL OF HEAVY METAL CATIONS FROM WATER WITH ISX*

Metal	*Initial conc., mg/l*	*ISX g*	*Residual conc., mg/l*	*Illinois discharge limit, mg/l*
Ag^{+}	53.94	0.32	0.016	0.005
Au^{3+}	30.00	0.50	<0.010	—
Cd^{2+}	56.20	0.64	0.012	0.050
Co^{2+}	29.48	0.64	0.090	—
Cr^{3+}	26.00	0.64	0.024	1.0
Cu^{2+}	31.77	0.32	0.008	0.020
Fe^{2+}	27.92	0.32	0.015	1.0
Hg^{2+}	100.00	0.64	0.001	0.0005
Mn^{2+}	27.47	0.64	0.015	1.0
Ni^{2+}	29.35	0.64	0.160	1.0
Pb^{2+}	103.60	0.64	0.035	0.100
Zn^{2+}	32.69	0.32	0.294	1.0

- Synthetic solutions (1,000 ml) containing the individual metals at the indicated concentrations were treated with the indicated amount of ISX (capacity = 1.56 meq metal ion/g) at pH = 3.7. Solutions were stirred for 5-60 min at a final pH of 8.9. After filtration, the residual metals were determined by a Varian Techtron AA 120. The theoretical weight of ISX for a divalent metal is 0.64 g. Value listed with less than (<) was below detection limit.

TABLE 2
REMOVAL OF METALS FROM DILUTE SOLUTION WITH ISX*

Metal	*Initial conc., mg/l*	*Residual conc., mg/l*
Cd^{2+}	5.62	0.001
Co^{2+}	2.95	<0.010
Cr^{3+}	2.60	0.026
Cu^{2+}	3.18	<0.005
Fe^{2+}	2.79	0.001
Hg^{2+}	10.00	0.0007
Mn^{2+}	2.75	0.010
Ni^{2+}	2.93	<0.050
Pb^{2+}	10.36	<0.031
Zn^{2+}	3.27	0.007

- A synthetic solution (1,000 ml) containing a mixture of heavy metals of the indicated concentrations at pH 3.5 was treated with ISX (capacity = 1.56 meq metal ion/g, 0.32 g) to a final pH = 8.9. After filtration the residual metals were determined by a Varian Techtron AA 120. Values with less than (<) were below detection limits.

ISX Treatment of Copper Etching Rinse Waters

Ammonium persulfate and alkaline [NH_4Cl/NH_4OH or $(NH_4)_2CO_3/NH_4OH$] etches are very useful in the printed circuit industry to etch copper from circuit boards. Several treatments for completely exhausted alkaline etch baths are known: (a) treatment with aluminum (11), (b) water dilution for copper carbonate precipitation (11), (c) caustic-heat treatment (11-13), and (d) acid sulfide treatment (14). The "Caper" process (1516) is effective in keeping the etching rate high by continuously removing the dissolved copper from ammonium persulfate etching baths. Rinse waters from these etching operations contain the $Cu(NH_3)_4^{2+}$ complex for which most conventional treatments are ineffective. Some recent reports (17-20) are available which show that these rinse waters are treatable.

ISX was evaluated (Figure 2) on several synthetic and industrial rinses and the copper concentration was

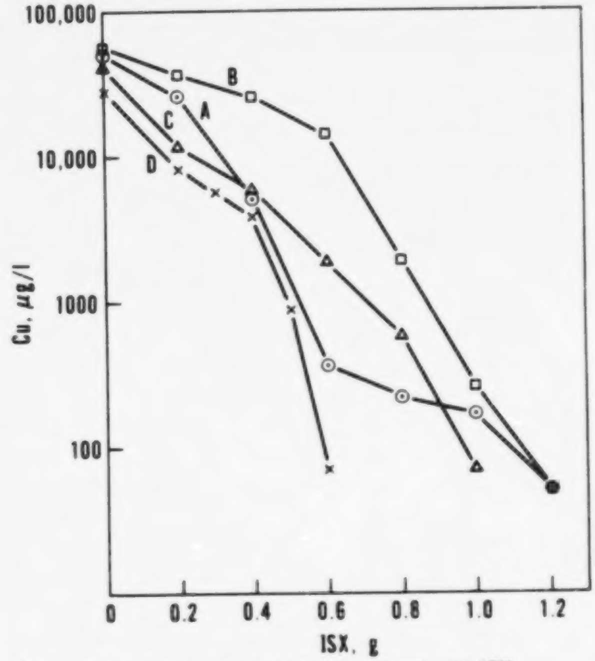

Figure 2. Copper ammonia complex removal with ISX.

Copper ammonia complex solutions (1,000 ml) were treated with increasing amounts of ISX (capacity = 1.5 meq metal ion/g). Aliquots (10 ml) of the supernatant were removed for copper analysis 5 min after each addition. Theoretical weight required is 1.02 g for the 50 mg/l copper ammonia solution.

Curve A. $Cu(NH_3)_4^{2+}$ standard solution (50 mg/l as Cu-initial); theoretical weight ISX reuuired is 1.02 g.

Curve B. $Cu(NH_3)_4^{2+}$ commercial rinse (53.63 mg/l Cu-initial); theoretical weight ISX required is 1.09 g.

Curve C. $Cu(NH_3)_4^{2+}$ commercial rinse (41.77 mg/l Cu-initial); theoretical weight ISX required is 0.85 g.

Curve D. $Cu(NH_3)_4^{2+}$ commercial rinse (28.35 mg/l Cu-initial); theoretical weight ISX required is 0.58 g.

lowered from 28-54 mg/l to less than 0.1 mg/l. ISX precoated on filters was also successfully evaluated for these rinses.

ISX Treatment of Other Copper Complexes

Copper in complexed form (EDTA, Quadrol, etc.) is very useful for electroless plating in alkaline solutions. Effective treatment of plating rinse waters from these plating baths has caused considerable problems. Recently we evaluated ISX for copper removal from these rinses and Figures 3-4 show the effectiveness of copper removal. Acidification of the rinse in the range of pH 3-6 assists in weakening or dissociating the bonds of the copper complex, allowing more complete removal (Figure 3). Figure 4 shows the copper removal using various amounts of ISX. The best results were always obtained when the rinse was adjusted to pH 3, ISX added, and pH readjusted to 3 (Quadrol).

Chromium (VI) Removal with ISX

Commercial anion exchange resins containing tertiary amine and quaternary ammonium groups are very useful in industrial wastewater treatment to remove heavy metal anions. Initial cost to install these exchange resin systems has limited the industrial application of this anti-pollution technique. The main reason for the high cost is that these resins are petrochemically based; because of the present petrochemical shortages, these products will likely increase in cost and may even be limited in supply.

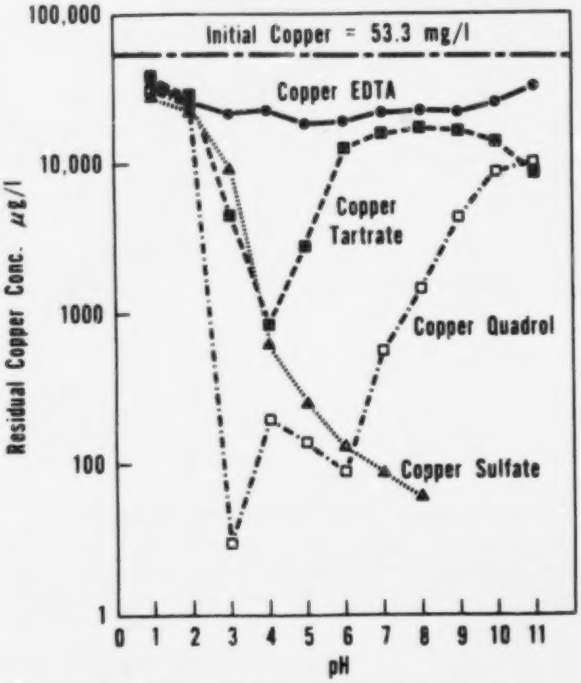

Figure 3. Treatment of copper complexes with ISX vs pH.

Solutions (1,000 ml) containing copper (53.3 mg/l) in complexed form were adjusted to the indicated pH. ISX (1.0 g, 1.5 meq metal/ion/g) was added and the pH was readjusted. After 30 minutes, aliquots were removed and filtered for residual copper analysis.

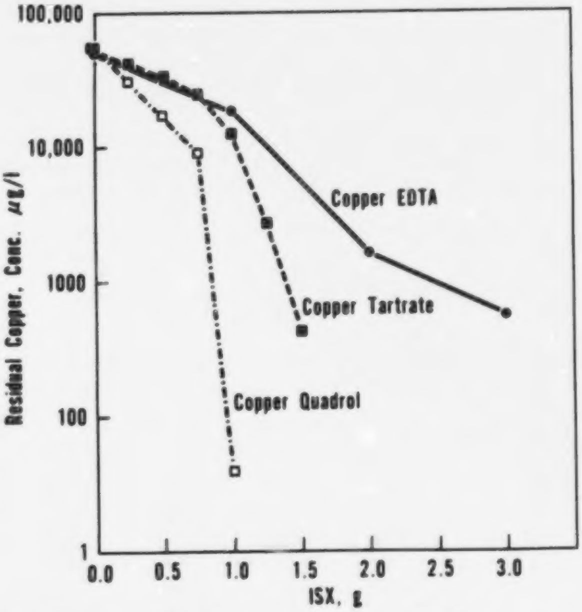

Figure 4. Treatment of copper complexes with ISX.

Solutions (1,000 ml) containing copper (53.3 mg/l) in complexed form were adjusted to pH 3 for quadrol, pH 4 for tartrate, and pH 5 for EDTA. ISX (1.5 meq metal ion/g) was added in the quantities shown. After 30 minutes, aliquots were removed and filtered for residual copper analysis.

A possible solution to this cost problem might be to use a naturally occurring, annually renewable, low-cost polymer such as starch. Previously we have shown that cationic starches were effective in chromium (VI) and ferro- and ferri-cyanide removal (8, 10).

The use of chromates and dichromates in plating and as corrosion control agents in cooling water systems is quite extensive. Chromium (VI) is very toxic and must be removed from industrial wastewaters before discharge. Chromium (VI) level allowed in waste effluents which are discharged to natural waterways has been established at a maximum concentration of 0.09 mg/l. Rinse waters of plating operations may vary in composition, but they usually contain 20-100 mg/l Cr^{6+} and have a pH of 2-3. These rinses are treated for three reasons: (a) pollution control, (b) water reuse, and (c) Cr^{6+} recovery.

Treatment for Cr^{6+} usually involves chemical reduction to Cr^{3+} with sulfur dioxide, sodium bisulfite, sodium metabisulfite, or ferrous salts at pH 2-3 (21-25). The Cr^{3+} is then precipitated at alkaline pH's as the hydroxide with caustic or lime. Nonreductive treatments of Cr^{6+} include anion exchange (26-31) and activated carbon (32).

ISX was evaluated in Cr^{6+} removal with surprising results. Since ISX and chromium (VI) species are both negatively charged, it would seem unlikely that any removal would occur. Figure 5 shows that optimum removal occurs below pH 3 after subsequent

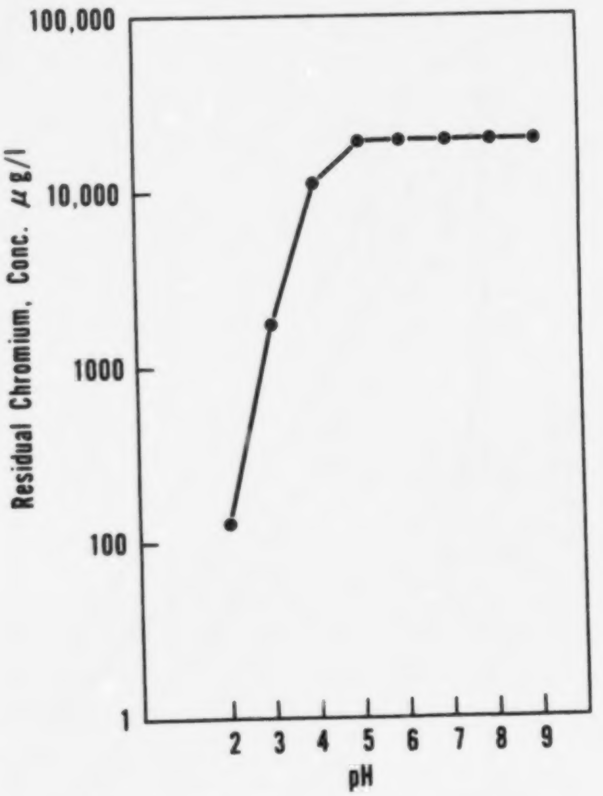

Figure 5. Effect of pH on chromium (VI) reduction with ISX.

Solutions (1,000 ml) containing chromate (20 mg/l as Cr^{6+}) were adjusted to the indicated pH. ISX (1.0 g, 1.5 meq metal ion/g) was added and the pH was readjusted. After 30 minutes, the pH was raised with caustic to 8.0 and aliquots were removed and filtered for chromium analysis.

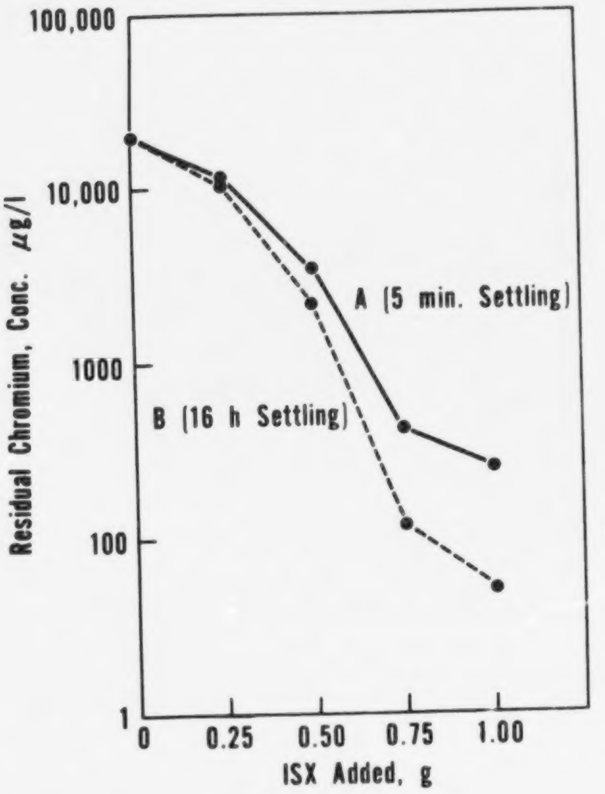

Figure 6. Effect on chromium (VI) removal of ISX.

Solutions (1,000 ml) containing chromate (20 mg/l as Cr^{6+}) were treated with the indicated amounts of ISX at pH 2.5. After 30 minutes, the solutions were adjusted to pH 8.0 with caustic and aliquots were removed and filtered for residual chromium analysis.

neutralization to pH 8. The following equation shows that in acidic media an oxidation-reduction occurs which allows chromium removal with ISX.

$$2CrO_4^{2-} + 16H^+ + \underbrace{6\,Starch\text{-}O\text{-}C\text{-}S^-}_{ISX} \rightarrow 2Cr^{3+} + 8H_2O + \underbrace{3(Starch\text{-}O\text{-}C\text{-}S)_2}_{Starch\ xanthide}$$

Upon neutralization to pH 8 with caustic, the chromium (III) is removed as the chromium (III) starch xanthate or chromic hydroxide. An advantage of this process is that as the pH is raised above 7 the starch xanthide reconverts into ISX to aid metal removal. Figure 6 shows the effectiveness of chromium (VI) removal with increasing amounts of ISX, whereas Figure 7 shows the rate of the chromium (VI) to chromium (III) reduction. Similar results were also obtained for dichromate and selenium removal with ISX.

ISX Case History Report

A plating company in the Northeast has been using ISX for 2 years as a filter precoat to treat rinse waters from three plating lines. Residual metal concentrations after the rinses are passed through the ISX-filters are copper (0.06 mg/l), nickel (0.57 mg/l), and tin-lead (0.33 mg/l-0.09 mg/l). The water is recirculated from the three filters back to the rinse tanks for reuse.

Two other systems have been designed using ISX: (1) copper-dye removal (4.75 million liters/day wastewater) and (2) copper-lignin removal (an 80-90° C wastewater of 100 mg copper/l at 1500 liters/minute and at pH 13-14).

ISX is commercially available in solid form by at least one supplier. Another company is promoting the on-site preparation of ISX to be used in conjunction with precoated filters for heavy metal removal. A 2-week evaluation last summer at a company discharging 0.2 mg Cu/l at 300 liters/minute showed a lowering to 0.01 mg Cu/l when ISX was incorporated. Incorporation of this ISX process at this plant would cost less than $600 for equipment and treatment facility modification. The weekly chemical cost would be approximately $10. Figure 8 shows that ISX has limited stability in solution, so it would have to be prepared every few days and then diluted daily for use.

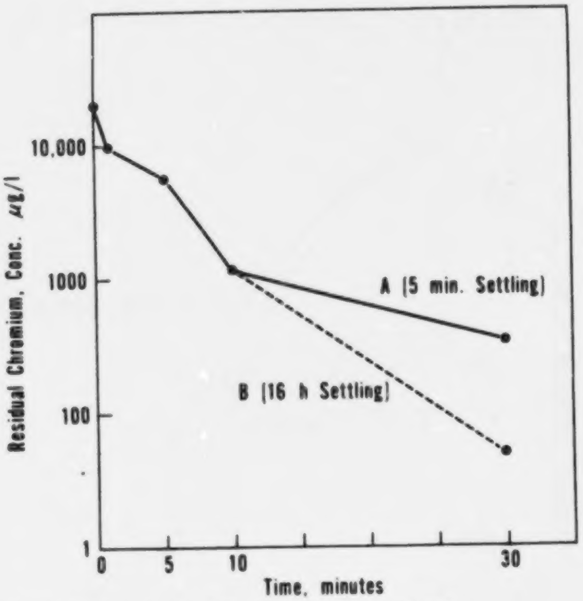

Figure 7. Chromium (VI) reduction rate with ISX.

Solutions (1,000 ml) containing chromate (20 mg/l as Cr^{6+}) and ISX (1.0 g, 1.5 meq metal ion/g) were stirred at pH = 2.5 for the indicated time. The solutions were adjusted to pH 8.0 with caustic and aliquots were removed and filtered for residual chromium analysis.

High pH-Lime Treatment of Electroless Copper Plating Rinse Waters

The electroless plating of copper on printed circuit boards and plastics is usually an autocatalytic formaldehyde reduction of a complexed alkaline copper (33-37). Suppliers to the plating industries use proprietary organic complexing agents for copper. For concentrated plating baths (37), treatments such as (a) raising the temperature to 50-65°C, (b) adding excess formaldehyde (1.5%) (38), (c) adding palladium activator (1-50 mg/l) (38), and (d) lowering the pH, have all been used successfully in decomposing the copper complexes. After plating is completed, it is necessary to rinse the plated articles. The rinse waters derived therefrom contain complexed copper which must be removed to prevent possible undesirable ecological effects as a result of introducing the copper to receiving waters or biological sewage treatment systems. These rinses usually contain 20-100 mg/l of copper as complexed copper around pH 10.9. Since usual chemical treatment is not effective on these rinse waters, special treatments are required and thus involve segregation of these solutions from the main process waters. Recently we reported a treatment method for the removal of copper from these complexed copper rinse solutions (20, 39, 40). Other reports have also appeared (41-46).

Our treatment involves the addition of a soluble calcium compound, i.e., calcium hydroxide, lime, calcium chloride, or calcium sulfate to rinse at a pH of 11.6-12.0 to precipitate copper hydroxide. The structure of the complexing agents determines the effectiveness of the treatment. The order of copper removal for several complexing agents is EDTA > NTA > HEDTA > NDA > tartrate ~ citrate > gluconate. The replacement of an acetate by a hydrogen or a hydroxyl diminishes removal of copper considerably. Tables 3 and 4 show some copper removal data from synthetic and actual industrial rinse baths.

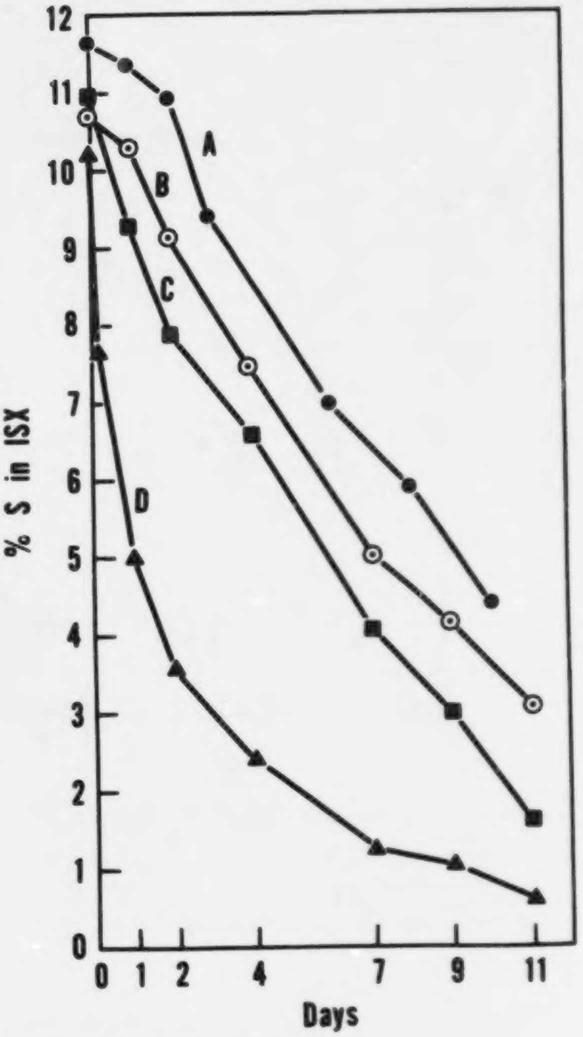

Figure 8. ISX storage stability in solution.

ISX samples were prepared and were stored under the following conditions. Samples were worked-up on the indicated days and the remaining capacity determined (as % S).

A. Reaction mixture as is.
B. Reaction mixture diluted with water.
C. Reaction mixture diluted with water and magnesium sulfate.
D. Isolated ISX reslurred.

Some general observations and comments about this treatment process are:

(a) Good removal is obtained over a pH range of 11.6-

TABLE 3
COPPER REMOVAL FROM COPPER-EDTA COMPLEX

Initial copper conc., mg/l*	*Calcium salt*	*Weight of salt, g*	*Final pH*	*Poly-mer mg/l*	*Residual† copper conc., mg/l*
50.0	CaO	0.50	11.6	1.5	0.14
50.0	$CaCl_2$	0.75	11.6	1.5	0.20
50.0	$CaSO_4$	0.92	11.7	1.5	0.44
50.0	$Ca(OH)_2$	0.50	11.7	1.5	0.09
5	$Ca(OH)_2$	0.50	11.7	1.5	0.10
100	$Ca(OH)_2$	1.00	11.6	1.5	0.06
1,910§	$Ca(OH)_2$	1.29	12.0	2.0	3.40

* Solutions (1,000 ml) of the indicated copper conc. were treated with the solid calcium compound. After stirring 5 min, the solutions were flocculated with polymer (anionic) and were filtered after 15 min settling.

† Determined using a Varian Techtron AA 120 spectrophotometer.

§ Stock solution (250 ml).

TABLE 4
COPPER REMOVAL FROM OTHER COPPER-COMPLEXES

*Complex**	*Initial† copper conc., mg/l*	*Calcium hydroxide, g*	*Final pH*	*Residual‡ copper conc., mg/l*
NTA	50	0.50	11.7	0.06
HEDTA	50	0.50	11.8	1.73
NDA	50	0.50	11.7	2.86
Tartrate	50	0.50	12.3	13.48
Citrate	50	0.50	12.1	9.01
Gluconate	50	0.50	11.8	23.88
A	50	0.46	11.7	0.32
B	50	0.48	11.7	12.03

* NTA = Nitrilotriacetic acid; HEDTA = N- Hydroxyethylethylenediaminetriacetic acid; NDA = Nitrilodiacetic acid; A = MacDermid sample; B = Shipley sample.

† Solutions (1,000 ml) were treated with solid calcium hydroxide. After stirring 5 min, the solutions were flocculated with polymer (anionic, 1.5 mg/l) and were filtered after 15 min settling.

‡ Determined using a Varian Techtron AA 120 spectrophotometer.

13.5 in the presence of excess calcium ion (greater than 2.5 moles calcium ion/1.0 mole copper).

(b) Treatment is effective over the temperature range of 20 - 60° C.

(c) Treatment is effective on concentrated baths as well as rinse solutions; however, it is ineffective on copper-Quadrol rinses.

(d) Use of an anionic polyelectrolyte (1.5 mg/l) aids in copper removal by promoting rapid settling.

(e) Analysis of the sludge shows it to be mainly copper hydroxide, except in the case of the tartrate rinse (calcium tartrate has limited solubility).

(f) Copper hydroxide sludge could be reprocessed to help defray cost of treatment.

(g) Treatment can be conducted batchwise and probably could be operated continuously.

(h) Chemical cost of treatment for a 50 mg/l copper-EDTA rinse with lime and polymer would be about $0.07/3,785 liters.

The supernatant after treatment would still contain a calcium complex which should have a much lower toxicity and could be biodegradable. If desired, the residual Ca^{++} in the treated rinse could be removed by carbonation with carbon dioxide, which would also give a concomitant lowering of pH and make the effluent more acceptable for discharge. Care should be taken in discharge of the calcium complex effluent, since the complexing agent will combine with other heavy metal ions if the pH is lowered when these segregated streams are treated further (i.e., in a clarifier with other process waters) or are discharged to streams or sewers. Oxidants, i.e., ozone-UV, could be used in decomposing the organic chelants to prevent recomplexation with other heavy metals. However, several recent reports (47-50) do show that copper in a complexed form, i.e., with EDTA, NTA, or pyrophosphate, is significantly less toxic than the free copper ion.

Formate, a byproduct of formaldehyde catalyzed electroless copper baths, does not interfere with copper removal in this proposed treatment and would remain soluble as calcium formate. The addition of small amounts of ISX (20), sulfide ion (43), dithiocarbamates (51), or mercaptobenzothiazole (52) after the lime treatment aids in further copper removal.

High pH-Lime Treatment Case History Report

Recently, an electroless copper plating rinse from a large company containing copper (173 mg/l) and nickel (51.9 mg/l) as the tartrate complex was evaluated in our laboratory. After treatment with high pH-lime, the residual copper was 0.3 mg/l and the nickel was 0.1 mg/l. These results were unexpected since treatment of standard copper tartrate complexes only resulted in 60-80% copper removal.

These results were reported to the company and, after similar success in their laboratory, the decision was made to install hardware for our high pH-lime treatment process (January 1977 start-up). They had evaluated at considerable expense reverse osmosis (RO), electrochemical, low pH-lime, sodium borohydride, and other techniques. They were using sodium borohydride reduction until the more economical and more effective high pH-lime treatment was installed. Presently, they use a premixed lime-calcium chloride slurry to have a higher calcium ion concentration, and they modify the mixture daily depending on the copper-nickel concentrations. Their electroless copper rinse water (40,000 liters/day) initially contains copper (50-300 mg/l) and nickel (0-150 mg/l); after the high pH-lime-polymer treatment to pH 11.5-12.0, the residual concentrations are 0.04-0.3 mg/l copper and 0.03-1.0 mg/l nickel, which satisfies the river discharge limit of 1.0 mg/l for each metal. The sludge is hauled away to an approved landfill.

Another company, using EDTA solutions to periodically backflush RO membranes after copper tartrate rinse water purification, is using the high pH-lime treatment for these process waters, and they report excellent copper removal. Initial copper concentrations (50-200 mg/l) are adjusted to pH 10-11.5 with caustic, lime is added to pH 12.3, and after anionic polyelectrolyte flocculation the residual copper concentration is <0.1 mg/l.

Ferrous Sulfate Treatment of Electroless Copper Rinse Waters

Since several electroless copper rinse waters from commercial baths (Quadrol-type) were untreatable by the high pH-lime method, we expanded our investigations to develop an effective treatment process for all types of electroless copper rinses (53). We found that if the pH of the rinse was lowered to where the complex dissociates, ferrous sulfate was added and the solution was neutralized to a pH greater than 9, effective copper removal was obtained (Table 5). This treatment is effective because the ferrous ion reduces Cu^{2+} to Cu^{+} and when the pH is raised the copper won't recomplex. Acidification assists in weakening or dissociating the bonds in the copper complex and this is evidenced sometimes by a color change in the rinse from pale blue to colorless. The color change is a useful guide to the amount of acid that would have to be added only to that pH. Several rinses have been required for the pH adjustment and if companies have rinses that turn colorless, acid treated effectively without prior acidification.

As the copper concentration of the rinse increases (10 mg/l to 1,000 mg/l), the Fe^{2+}/Cu^{2+} ratio can be lowered from 8.0 to 1.0 for effective treatment. This fact is especially important from an economic point of view. Since several companies are going more to counter flow rinsing techniques for water use reduction, the copper complex concentration will increase in these rinses, so more effective utilization of ferrous sulfate will be realized. The use of lime or sodium hydroxide as neutralization agents (Table 5) were equally effective in copper and iron removal; however, the use of sodium hydroxide in our investigations gave lower dissolved solids and less sludge. A 5-minute ferrous sulfate contact time was usually sufficient for good copper removal. As long as the pH was raised above 9.0 (Table 6), the copper

TABLE 5

COPPER REMOVAL FROM COPPER-QUADROL COMPLEX—DETERMINATION OF AMOUNT OF FERROUS SULFATE REQUIRED AND EFFECT OF BASE*

Copper conc., mg/l	*Adjusted pH*	*$FeSO_4 \cdot 7H_2O$, g*	*Fe^{2+}/Cu^{2+}*	*Base*	*Residual copper conc.,§ mg/l*	*Residual iron conc.,§ mg/l*
50	2.7	0.3	1.2	$Ca(OH)_2$	33.0	4.74
50	2.7	0.4	1.6	$Ca(OH)_2$	15.5	8.70
50	2.7	0.5	2.0	$Ca(OH)_2$	0.58	9.46
50	2.7	0.75	3.0	$Ca(OH)_2$	0.16	5.68
50	2.7	1.0	4.0	$Ca(OH)_2$	0.01	2.68
50	2.7	0.5	2.0	NaOH	1.25	8.42
50	2.7	0.75	3.0	NaOH	0.22	4.54
50	2.7	1.0	4.0	NaOH	0.05	5.16
50	9.5‡	0.5	2.0	$Ca(OH)_2$	0.44	6.38
50	7.8	0.75	3.0	$Ca(OH)_2$	0.01	6.70
50	7.2	1.00	4.0	$Ca(OH)_2$	0.01	7.41
50	7.2§	1.00	4.0	$Ca(OH)_2$	0.09	3.06
10	2.7	0.20	4.0	$Ca(OH)_2$	6.60	0.49
10	2.7	0.30	6.0	$Ca(OH)_2$	1.42	1.52
10	2.7	0.40	8.0	$Ca(OH)_2$	0.07	1.00
10	5.4‡	0.20	4.0	$Ca(OH)_2$	1.00	1.48
1000	2.7	3.0	0.6	$Ca(OH)_2$	421.0	27.5
1000	2.7	4.0	0.8	$Ca(OH)_2$	147.0	85.0
1000	2.7	5.0	1.0	$Ca(OH)_2$	0.36	12.5

* Copper-Quadrol solutions (1,000 ml) containing the indicated copper concentration at pH 10.6-11.9 were acidified with 1N H_2SO_4 to pH 2.7. Ferrous sulfate was added as a solid and after 5 min, the pH was raised to 11.2 with the base listed. Nalcolyte 676 (2.5 mg/l) anionic polyelectrolyte was added and the solutions were allowed to settle 5 min before filtering.

† Determined using a Varian Techtron AA 120 spectrophotometer.

‡ No acid added, pH lowering due to ferrous sulfate addition.

§ Solution lowered to pH 2.7 after ferrous sulfate addition.

removal was excellent; however, to lower the residual iron to low values the pH had to be raised to 11.7.

The ferrous sulfate treatment was evaluated on solutions containing different synthetic copper complexes (Table 7) and several commercial rinses (Table 8) with excellent copper removal. The use of anionic polyelectrolytes (1.0-2.5 mg/l) was very effective in the flocculation and settling of the sludge. Even though we evaluated only batch treatment, the method could be operated continuously. The chemical cost of treatment for a 50 mg/l copper-Quadrol type rinse with sulfuric acid, ferrous sulfate, lime, and polymer would be about $0.36/3,785 liters.

TABLE 6
EFFECT OF FINAL pH* ON COPPER REMOVAL FROM COPPER-QUADROL COMPLEX

Adjusted pH	*Final pH*	*Residual copper conc.,† mg/l*	*Residual iron conc.,† mg/l*
2.7	7.0	0.24	25.4
2.7	9.0	0.17	10.5
2.7	11.0	0.14	4.5
2.7	11.7	0.05	0.31
6.4‡	7.0	1.34	48.6
6.4‡	9.0	0.01	13.8
6.4‡	11.0	0.01	1.4
6.4‡	11.7	0.01	0.23
9.0§	9.0	0.01	14.1
9.0§	11.0	0.01	1.9
9.0§	11.7	0.01	0.17

* Dilute 39.0 ml copper-Quadrol stock solution to 1l (50 mg Cu/l) and then adjust the solutions to the desired pH with 1N H_2SO_4. Treat solutions with ferrous sulfate ($FeSO_4 \cdot 7H_2O$, 1.0 g) for 5 min, add calcium hydroxide to the indicated pH and add Nalcolyte 676 (2.5 mg/l) for flocculation. After settling 5 min, an aliquot (10 ml) was filtered through Whatman 54 filter paper for analysis.

† Copper and iron concentrations were determined using a Varian Techtron AA 120 spectrophotometer.

‡ Adjusted to pH 7.0 with acid, then to pH 6.4 with ferrous sulfate.

§ Adjusted to pH 9.0 with ferrous sulfate.

Ferrous Sulfate Treatment Case History Report

Two printed circuit shops are presently using this method for treating electroless copper and alkaline etch rinses. A large West Coast PC manufacturer batch treats 1,200 liters/day of a MacDermid C rinse and also floor spills from electroless plating and alkaline etchant baths with 5-20 g/l ferrous sulfate to pH 10.8. After polymer flocculation (3.0 mg/l), the residual copper concentration averages 0.1 mg/l while the residual iron concentration is below 1.0 mg/l. This company is presently installing a continuous flow ferrous sulfate treatment for their more dilute electroless copper rinses.

An East Coast PC manufacturer treats six electroless copper rinses and one alkaline etchant rinse with ferrous sulfate in a continuous flow system. The 100 liters/minute flow of 20-30 mg copper/l consistently averages less than 1 mg copper/l after treatment.

Both companies report less volume of sludge than the previous treatments they were using.

Spent Pickle Liquor Treatment of Copper Complexes

Recently (54) we found that spent pickle liquor gave excellent copper removal when substituted for ferrous sulfate in the previous treatment. The "pickling" process is the removal of oxide scale from steel products by immersion in hot acid solution. Spent liquor from batch steel processing contains between 0.5 - 2% by weight free acid and 5.8 - 8% by weight ferrous ion, while from continuous steel processing between 4 - 7% by weight free

TABLE 7
COPPER REMOVAL FROM SYNTHETIC COPPER COMPLEXES WITH FERROUS SULFATE TREATMENT*

Complex	*Initial copper conc., mg/l*	*2N H_2SO_4, ml*	*pH for colorless† solution*	*$FeSO_4 \cdot 7H_2O$, g*	*$Ca(OH)_2$, g*	*Residual copper conc., mg/l*	*Residual iron conc., mg/l*
EDTA	50	3.8		1.0	1.16	0.23	0.12
	10	0.8		0.4	0.94	0.28	0.10
NTA	50	2.2		1.0	1.26	0.29	0.11
	10	0.7		0.4	0.44	0.09	0.11
Tartrate	50	8.0	4.5-4.8	1.0	1.54	0.75	0.21
	10	2.0		0.4	0.64	0.35	0.29
Gluconate	50	2.5	4.5-4.7	1.0	0.88	0.82	32.70
	10	0.7		0.4	0.53	0.09	6.20
Citrate	50	4.8	4.0	1.0	0.76	0.01	0.28
	10	1.8		0.4	0.45	0.02	0.18
Triethanol Amine	50	6.0	5.5	1.0	1.04	0.11	24.48
	10	1.5		0.4	0.64	0.53	8.33
Quadrol	50	5.9	3.0	1.0	0.73	0.01	2.68
	10	1.3		0.4	0.51	0.07	1.00

* Solutions (1,000 ml) containing the copper complexes at the indicated concentrations were acidified with 2N H_2SO_4 to pH 2.7. The indicated amount of ferrous sulfate was added and the solution stirred for 5 min. Calcium hydroxide was added to raise the pH to 11.7 and the solutions were flocculated with Nalcolyte 676 (2.5 mg/l) anionic polymer. After settling the solutions were filtered for analysis.

† pH values listed is where copper complex dissociates. When no value is listed, the blue complex does not dissociate above pH 1.8

TABLE 8
COPPER REMOVAL FROM COMMERCIAL COPPER COMPLEXES WITH FERROUS SULFATE TREATMENT*

Bath	*Initial copper conc., mg/l*	*$2N H_2SO_4$, ml*	*pH for colorless† solution*	*$FeSO_4 \cdot 7H_2O$, g*	*$Ca(OH)_2$, g*	*Residual copper conc., mg/l*	*Residual iron conc., mg/l*	*Dissolved‡ solids, mg/l*
MacDermid								
A	50	---		1.0	1.42	0.02	7.1	---
A	10	---		0.4	0.46	0.02	2.3	---
B	50	15.0	2.7-3.0	1.0	1.69	0.17	17.8	---
B	10	4.7		0.4	0.50	0.08	6.3	---
C	50	19.0		1.0	2.18	0.09	21.0	---
C	10	6.0		0.4	0.60	0.03	5.9	---
Shipley								
A	50	4.0	4.8	1.0	0.56	0.33	0.53	---
A	10	1.6		0.4	0.27	0.21	0.47	---
B	50	4.5	2.8	1.0	0.61	0.27	24.86	---
B	10	1.1		0.4	0.26	0.31	2.78	--
C	50	8.2	3.9	1.0	0.94	0.20	14.17	---
C	10	1.8		0.4	0.27	0.11	2.72	---
D	50	3.5	3.8	1.0	0.51	0.12	6.94	1,750
D	10	1.7		0.4	0.34	0.20	1.47	720
D	50	---		---	---	---	---	817
D	50	3.5		1.0	0.92	0.08	6.85	2,320
D	50	3.5		1.0	20.5 ml§	0.16	8.88	2,064

* Solutions (1,000 ml) containing the copper complexes at the indicated concentrations were acidified with 2N H_2SO_4 to pH 2.7. The indicated amount of ferrous sulfate was added and the solution stirred for 5 min. Calcium hydroxide was added to raise the pH to 11.7 and the solutions were flocculated with Nalcolyte 676 (2.5 mg/l) anionic polymer. After settling the solutions were filtered for analysis.

† pH values listed is where copper complex dissociates. When no value is listed, the blue complex does not dissociate above pH 1.8.

‡ Filtered samples were evaporated to dryness, oven dried at 125° C, cooled, and weighed.

§ Sodium hydroxide (1N).

TABLE 9
SPENT PICKLE LIQUOR TREATMENT OF QUADROL-BASED ELECTROLESS COPPER PLATING RINSE WATERS*

Initial copper conc., mg/l	*Initial pH*	*Pickle liquor, ml*	*Neutralization agent*	*Final pH*	*Residual copper conc., mg/l*
50	11.2	10.6	NaOH	11.4	0.05
50	11.2	10.6	$Ca(OH)_2$	11.3	0.04
500	11.6	32.0	NaOH	11.4	0.44
500	11.6	32.0	$Ca(OH)_2$	11.2	0.21
1000	12.0	53.0	NaOH	11.4	0.50
1000	12.0	53.0	$Ca(OH)_2$	11.4	0.31

* Solutions (1000 ml, 50-1000 Cu/l) were treated with the indicated amounts of pickle liquor (18.8 g/l ferrous ion) at pH 2.5 for 15 minutes. The solutions were neutralized with sodium hydroxide (5N) and/or lime (solid) to the indicated pH and then flocculated with anionic polymer (2.5-5.0 mg/l). The samples were filtered through filter paper for analysis, using atomic absorption spectrometry.

TABLE 10
SPENT PICKLE LIQUOR TREATMENT OF COPPER-AMMONIA ETCHANT RINSE WATERS*

Initial copper conc., mg/l	*Pickle liquor, ml*	*Final pH*	*Residual copper conc., mg/l*
50	2.65	11.7	15.66
50	5.30	11.7	27.21
50	7.45	11.7	0.65
50	10.6	11.7	0.37
50	10.6	9.4	3.88
50	10.6	10.0	0.57
50	10.6	11.0	0.41
50	10.6	11.3	0.15

* Solutions (1000 ml, 50 mg Cu/l) were treated with the indicated amounts of pickle liquor (18.8 g/l ferrous ion) at pH 9.4 for 15 minutes. The solutions were neutralized with sodium hydroxide (5N) to the indicated pH and the flocculated with anionic polymer (2.5 mg/l). The samples were filtered through filter paper for analysis, using atomic absorption spectrometry.

acid and 5.1 - 5.9% by weight ferrous ion. Since spent pickle liquor has little commercial value, our process would give a possible advantageous use for some of the 2-4 billion liters of spent pickle liquor produced annually. Tables 9-10 show the effectiveness of spent pickle liquor on a copper-Quadrol and a copper-ammonia etchant rinse. Approximately 11 liters of spent pickle liquor (6.6% by weight ferrous ion) would be required to treat 3,785 liters of a 50 mg/l copper quadrol or copper-ammonia rinse.

Treatment of Electroless Nickel Rinse Waters

The electroless deposition of nickel is commercially the most widely used of the electroless processes. Numerous articles (34, 55-66) are available which describe the chemistry and operating conditions of this controlled autocatalytic reduction of nickel. Both acidic (pH 4-6) and alkaline (pH 8-10) formulations are used containing nickel salt ($NiSO_4$ or $NiCl_2$), reducing agent (NaH_2PO_2 or $NaBH_4$), chelating agent (citrate or glycolate) and pH control agent (H_2SO_4-NH_4Cl or NH_4OH-NH_4Cl). Because of the large number of electroless nickel plating formulations described in the literature, only a few synthetic baths were prepared and evaluated for treatment. Several commercial baths were also evaluated.

Very little has been published (67-68) on the treatment of electroless nickel process waters. Our preliminary evaluations to see what effect caustic and lime treatments have on rinse waters revealed that electroless nickel rinse waters could be treated this way. Tables 11-13 show that low residual nickel concentrations can be attained with either a caustic or lime treatment at high pH and at various nickel concentrations. Even though the volume of sludge is greater with the lime treatment, the polymer-treated floc settles faster and is more easily removed than when caustic is used. Another apparent advantage of using lime is the removal of some of the decomposition product of the reducing agents used in the plating. Hypophosphite and borohydride decompose according to the following equations to yield orthophosphite and metaborate which form only slightly soluble calcium

$$Ni^{2+} + H_2O + H_2PO_2^- \rightarrow H_2PO_3^- + 2H^+ + Ni^0$$

$$4Ni^{2+} + 8OH^- + BH_4^- \rightarrow BO_2^- + 6H_2O + 4Ni^0$$

salts, allowing them to be precipitated.

We found (69) that in the treatment of some of the formulations, a longer contact time at high pH gave lower residual nickel values. Acid baths contain compositions having less buffering action (NH_4^+ NH_3), and considerably less base is needed to adjust the pH. Also, the acid bath rinse waters for the most part allowed better nickel removal at a lower pH (11 vs 12.5) and gave a faster settling sludge. However, preliminary results in treating rinse waters from an acidic (pH 5.4) Shipley bath showed the best results at high pH (12.5) with long contact times (2-16 h).

TABLE 11
NICKEL REMOVAL FROM SYNTHETIC ELECTROLESS NICKEL BATHS*

Bath†	*$Ca(OH)_2$ added, g*	*Final pH*	*Residual nickel conc., mg/l*
A	0.35	10.0	39.74
	0.49	11.0	3.49
	0.78	12.0	0.50
	1.25	12.5	0.44
		16 h settling	0.13‡
	1.25	12.5	0.12§
B	0.10	9.9	0.07
	NaOH	9.5	0.24
C	0.09	10.0	50.00
	0.16	11.0	50.00
	0.49	12.0	2.69
	1.47	12.5	0.54
		16 h settling	0.24‡
	1.47	12.5	0.15§
D	0.23	10.0	50.00
	0.43	11.0	50.00
	0.78	12.0	50.00
	1.98	12.5	42.00
	1.98	12.5	42.00
		16 h settling	0.12‡
	1.98	12.5	0.18§

* Solutions (1,000 ml, 50 mg Ni/l) were treated with the indicated amounts of calcium hydroxide for 15 minutes and then flocculated with Nalcolyte 676 (5 mg/l). Samples were then filtered for analysis.

† A = $NiCl_2 \cdot 6H_2O$ (50 g), $NaH_2PO_2 \cdot H_2O$ (10 g), glycolic acid (56 ml) in water to total volume of 1 l, at pH = 4.2; B = $NiCl_2 \cdot 6H_2O$ (30 g), $NaH_2PO_2 \cdot H_2O$ (10 g), glycolic acid (56 ml) in water total volume of 1 l, at pH = 4.2; C = Bath A composition with no pH (4.2) adjustment; D = $NiCl_2 \cdot 6H_2O$ (45 g), $NaH_2PO_2 \cdot H_2O$) (16 g), Na_3 citrate · $2H_2O$ (82 g), NH_4Cl (50 g) in water adjusted to pH 8.9 with NH_4OH and a total volume of 1 l.

‡ Solutions adjusted to pH 12.5 were allowed to settle 16 h and reanalyzed.

§ Solutions were stirred at pH 12.5 for 2 h and then flocculated with polymer. Samples were filtered for analysis.

TABLE 12
EVALUATION OF $Ca(OH)^2$ AND NaOH FOR NICKEL REMOVAL FROM MACDERMID A ELECTROLESS NICKEL RINSE WATERS*

Initial nickel conc., *mg/l*	*$Ca(OH)_2$ added, g*	*Final pH*	*Residual nickel conc., mg/l*	*NaOH (5N), ml*	*Residual nickel conc., mg/l*
10	0.04	10	10.00	---	---
10	0.11	11	10.00	0.6	6.38
10	0.35	12	0.25	2.4	1.76
10	1.60	12.5	0.20	10.4	0.18
50	0.17	10	25.00	---	---
50	0.59	11	6.87	1.0	26.92
50	0.85	12	1.88	3.8	4.50
50	2.49	12.5	0.61	14.2	0.23
500	1.33	11	39.20	8.0	81.24
500	2.73	12	30.20	20.0	42.85
500	4.93	12.5	27.75	35.0	21.53

* Solutions (1,000 ml) containing the indicated nickel concentrations from a MacDermid A electroless nickel plating bath at pH 8.6 were treated with the indicated amounts of $Ca(OH)_2$ or NaOH(5N). After a 30 minute contact time, the solutions were flocculated with Nalcolyte 676 (2.5 mg/l) and then analyzed for residual nickel.

Electroless Nickel Case History Report

A large Midwestern company using an OMI-Udylite A electroless nickel plating bath containing Ni^{2+}, hypophosphite, citrate, and ammonia for plating on plastics has installed the previously described high pH-lime-caustic treatment. A previous treatment tried by the company using phosphoric acid and then caustic was unsuccessful as some of the nickel-ammonia complex was undestroyed. The company treats 30,000 liters/day (85-140 mg/l nickel) of a dragout rinse (pH 8.6) with lime (45.4 kg) to pH 9.5-10.0 for 1 hour with agitation. Caustic (22.7 kg as pellets) is added to adjust the pH to 12.0-12.5. A 1% solution of a Benchmark Separaid-10 anionic polymer (12.5 mg/l) is added for flocculation. The sludge is settled for 2-3 hours and the supernatant (less than 0.5 mg/l residual nickel) is pumped off and discharged. The sludge is removed weekly from the pit and filter pressed. This treatment has allowed this company to lower their nickel discharge to a zero flow stream from 3.2 kg/day to 0.014 kg/day. Eventually, they would like to install carbon and ion exchange columns for further effluent treatment and complete water reuse. Even though our laboratory treatments on OMI-Udylite A (new bath) rinse waters were only 95-98% effective, the on-site treatment by this company has always proved to be 96-99% effective and sometimes 100% effective on spent rinse waters.

TABLE 13
EVALUATION OF Ca(OH)² AND NaOH
FOR NICKEL REMOVAL FROM MACDERMID B
ELECTROLESS NICKEL RINSE WATERS*

Initial nickel conc., mg/l	*$Ca(OH)_2$ added, g*	*Final pH*	*Residual nickel conc., mg/l*	*NaOH (1N), ml*	*Residual nickel conc., mg/l*
10	0.01	9	5.68	0.4	4.50
10	0.03	10	1.59	0.7	1.10
10	0.04	11	0.51	2.5	0.05
10	0.18	12	0.49	3.8	0.05
50	0.08	9	0.49	2.6	2.53
50	0.13	10	0.44	3.9	0.19
50	0.16	11	0.05	6.4	0.21
50	0.32	12	0.02	24.4	0.12
500	0.82	9	2.27	37	6.57
500	0.97	10	0.69	45	2.47
500	1.12	11	0.30	54	2.80
500	1.56	12	0.29	81	1.41

* Solutions (1,000 ml) containing the indicated nickel concentrations from a MacDermid B electroless nickel bath at pH 4.7 were treated with the indicated amounts of $Ca(OH)_2$ or NaOH(1N). After a 30 minute contact time, the solutions were flocculated with Nalcolyte 676 (2.5 mg/l) and then analyzed for residual nickel.

Treatment Process for Copper Pyrophosphate Electroplating Rinse Waters

Copper plating in alkaline media with the copper pyrophosphate complex anion has been known for over 125 years; however, it only gained commercial importance about 35 years ago (70-71). Numerous articles have appeared disclosing bath formulations, operating conditions, and applications (72-76); however, very little information is available on the treatment of copper pyrophosphate rinse waters (77-79).

After the articles are plated, they go into a dragout or stagnant rinse tank and through a series of flowing rinses. The dragout rinse usually is added back to the plating bath for makeup water. The flowing rinse water containing $Cu(P_2O_7)_2^{6-}$, $P_2O_7^{4-}$, and HPO_4^{2-} has to be treated before discharge to meet the ever more stringent standards.

TABLE 14
Ca(OH)² TREATMENT OF ACTUAL COPPER PYROPHOSPHATE ELECTROPLATING RINSES*

Rinse	*Initial Cu conc., mg/l*	*Initial pH*	*Initial $P_2O_7^{4-}$ conc., mg/l*	*Initial HPO_4^{2-} conc., mg/l*	*$Ca(OH)_2$, mg*	*Residual Cu conc., mg/l*	*Residual P conc., mg/l*	*Residual Ca conc., mg/l*	*Final pH*
A	67.36	8.9	728.7	45.0	992	0.02	0.2	30.2	11.4
B	74.50	8.1	686.7	347.8	1,387	0.04	0.6	14.3	11.5
C	70.84	7.7	893.6	668.7	2,124	2.54	3.1	3.6	11.4
A	50	8.6	539	33.4	734	0.02	0.2	27.4	11.1
B	50	8.0	460	233	929	0.01	0.2	19.7	11.2
C	50	7.7	625	468	1,487	0.02	0.2	44.7	11.3
A	10	8.4	108	6.7	147	0.01	0.2	---	10.6
B	10	8.1	92	47	186	0.01	0.2	---	10.8
A	100	8.7	1,078	67	1,470	0.02	0.2	---	11.6
B	100	8.1	920	466	1,860	0.02	0.2	---	11.6
A	50	8.6	539	33.4	550 (as lime)	0.01	0.2	---	11.1

* Copper pyrophosphate rinse solutions (1,000 ml) containing the indicated concentration were treated with calcium hydroxide. After stirring for 5 min, anionic polyelectrolyte (Dow A-23, 5 mg/l) was added and residual copper, calcium, and phosphorous were determined after filtration.

TABLE 15

$Ca(OH)^2$-$CaCl^2$ TREATMENT OF ACTUAL COPPER PYROPHOSPHATE ELECTROPLATING RINSES*

Rinse	*Initial Cu conc., mg/l*	*Initial pH*	*Initial $P_2O_7^{4-}$ conc., mg/l*	*Initial HPO_4^{2-} conc., mg*	*$Ca(OH)_2$, mg*	*$CaCl_2$ mg*	*Residual Cu conc., mg/l*	*Residual P conc., mg/l*	*Residual Ca conc., mg/l*	*Final pH*
A	67.36	8.9	728.7	45.0	925	97	0.02	0.3	25.4	11.4
B	74.50	8.1	686.7	347.8	872	751	0.01	0.2	10.2	11.4
C	70.84	7.7	893.6	668.7	1,135	1,444	0.01	0.2	37.2	11.1
A	50	8.6	539	33.4	685	72	0.02	0.2	16.1	11.2
B	50	8.0	460	233	584	503	0.01	0.2	16.7	11.1
C	50	7.7	625	468	794	1,011	0.02	0.2	31.5	11.1

* Copper pyrophosphate rinse solutions (1,000 ml) containing the indicated concentration were treated with calcium hydroxide and calcium chloride. After stirring for 5 min, anionic polyelectrolyte (Dow A-23, 5 mg/l) was added and residual copper, calcium, and phosphorous were determined after filtration.

Preliminary experiments showed that good copper hydroxide removal (50 mg/l copper lowered to 0.44 mg/l) was obtained by adjusting copper pyrophosphate rinse waters to pH 12.2 with caustic; however, no pyrophosphate or orthophosphate removal was observed. Since strict phosphorus discharge standards have to be met, an alternate treatment was sought. It is well known that cations such as Ca^{2+}, Mg^{2+}, Zn^{2+}, Al^{3+} and Fe^{3+} form insoluble precipitates with HPO_4^{2-} and $P_2O_7^{4-}$ when an excess of cation is present (80-88). Since calcium hydroxide, lime, and calcium chloride are economical sources of Ca^{2+}, they were chosen for this study. As the Ca^{2+} is added to the rinse, it complexes with the HPO_4^{2-} and excess $P_2O_7^{4-}$ and precipitates them as their insoluble calcium salts. When the excess $P_2O_7^{4-}$ is removed, the copper probably precipitates as $Cu_2P_2O_7$.

The copper pyrophosphate baths and rinses evaluated were from the printed circuit industry which uses these baths for through-hole-plating of printed circuit boards. Since occasional analysis (89-90) for copper, pyrophosphate, orthophosphate, and ammonia is required for control purposes to keep the bath in good operating condition, the plater knows the relative concentrations of pyrophosphate and orthophosphate in his rinses. Using this analysis information, a treatment process has been designed to lower copper and phosphorous concentrations of synthetic and actual rinse waters. The treatment process can be modified as the orthophosphate concentration builds up. New baths will contain very little orthophosphate, and treatment of these rinses with calcium hydroxide or lime at pH's above 9 will give excellent copper and phosphorous removal. As the orthophosphate concentration builds up to greater than 90 g/liter, the substitution of some calcium chloride for lime will be required to get more Ca^{2+} into solution for excellent precipitation.

Some experimental results for this treatment are shown in Tables 14 and 15. Some general observations and comments about this treatment process are:

(a) Good removal is obtained over a pH range of 9.0-11.5 in the presence of excess calcium ion.

(b) To lower the copper concentration to less than 0.02 mg/l and phosphorous concentration to less than 1 mg/l, 3.0 mmoles Ca^{2+} is required for each mmole of $P_2O_7^{4-}$ and 2.0 mmoles Ca^{2+} is required for each mmole of HPO_4^{2-}.

(c) Rinses containing high orthophosphate concentrations should be treated with higher proportions of calcium chloride for greater Ca^{2+} solubility.

(d) Use of an anionic polyelectrolyte (3-5 mg/l) aids sludge settling.

(e) Treatment can be conducted batchwise and probably could be operated continuously.

(f) Chemical cost treatment using lime and polymer for a copper pyrophosphate rinse containing Cu^{2+} (54 mg/l), $P_2O_7^{4-}$ (500 mg/l), and HPO_4^{2-} (250 mg/l) would be about $0.16/3,785 liters.

Copper Pyrophosphate Case History Report

A large tool manufacturer in the Southwest uses copper pyrophosphate baths for carburizing parts. The rinse waters (40-50 mg/l copper, 40 liters/minute) up until a few months ago were not segregated and were treated with other process waters. This company now segregates the rinse waters for treatment with caustic at pH 12.2. This practice enables them to meet their copper discharge limits and, since they discharge to a sewer, their phosphorus level is below discharge limits. However, they are having problems filtering the copper hydroxide floc and will have to meet stricter phosphorous limits; therefore, they are evaluating the lime treatment.

The mention of firm names or trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over other firms or similar products not mentioned.

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An Overview of the Sludge Disposal Problem

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This discussion covers an overview of the sludge disposal problem as it affects the metal finishing industry. It reviews briefly the Federal legislation that has had an impact on the industry and points up the problems and responsibilities facing both the Government and industry and shows, in particular, that their goals are not in conflict. The discussion covers the basic problems, minimizing costs by the manufacturer, and minimizing regulatory overkill. Illustrations cover the effect of solids concentration on sludge volume, concentrations achievable with various dewatering methods, basic problems in sludge disposal, and disposal costs.

INTRODUCTION

The problems that have been encountered with the disposal of industrial sludges do not come as a surprise. From the time the Federal Water Pollution Control Act (Public Law 92-500) was passed 6 years ago disposing of the residues from industrial wastewater treatment systems has been a constant concern. Since 1972 the problem has been continually discussed in both industrial and Governmental sectors. In general, the goal of cleaning the nation's wastewater discharges is being met, but the problems of disposing of residues from wastewater treatment systems are just beginning to be studied in the systematic manner needed to prevent wastage of large amounts of resources.

From the environmental point of view, there must be assurances that the residues removed from the wastewater at great cost and effort are not reintroduced into the environment in a harmful manner. On the other hand, the manufacturer, having already paid a significant sum for a wastewater treatment system, must keep any additional costs for sludge disposal at the lowest possible level necessary to protect the environment.

These two views are not necessarily in conflict. However, sound scientific data needed to reach a reasoned judgment on just what is required is lacking. The fate and the effect of many pollutants in industrial sludges are not sufficiently understood to allow quantitative decisions to be made.

With the passage of Public Law 94-580, the Resource Recovery and Conservation Act, however, the legislative noose is tightening. This law is not necessarily bad for industry. There has been so much confusion relating to the relative dangers of some industrial sludges that in some instances we have seen some stringent restrictions on the disposal of all industrial sludges.

The problem of sludge disposal is especially troublesome for manufacturers who are discharging to a municipal wastewater system and who are forced to pretreat their wastes. Space for onsite disposal is usually limited and the manufacturing facilities are often too small to support a sludge concentration system of sufficient capability to make hauling relatively economical. However, once again, close control of *truly* hazardous sludges may pave the way toward a reasonable approach for those sludges which are not hazardous or which can be disposed of in a non-hazardous manner.

During the discussion on Public Law 94-580, you have seen that industrial sludges were broadly classified as solid wastes. The section of the law that is most significant, however, concerns hazardous wastes. By Spring of 1978, EPA must promulgate hazardous waste regulations. But EPA must first establish criteria for defining these wastes, "taking into account toxicity, persistence, and degradability in nature, potential for accumulation in tissue, and other related factors, such as flammability and corrosiveness." Therefore, the definition finally arrived at by EPA as to what materials constitute hazardous wastes will be critical in determining disposal methods.

The criteria currently being developed for use in defining a substance as "hazardous" address such wastes as:

- Flammable
- Corrosive
- Reactive
- Infectious
- Radioactive, and
- Toxic.

Methods for determining if a material falls under any of these categories are being developed. From the preliminary draft, wastes containing lead, zinc, copper or cyanide would be considered hazardous—thus it appears that the electroplating waste treatment residues will be

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treated as hazardous in the implementation of the law.

The act also provides financial assistance to states for solid waste management and encourages states to adopt and enforce regulations that would be equivalent to the Federal Government's. In fact, great emphasis is placed on putting control in the hands of the States.

The Basic Problem

As stated earlier, the goals of industry and the regulators are not necessarily in conflict. If there were a sound scientific basis for controlling wastewater treatment sludges from the electroplating industry that did not result in substantial added costs needed to provide a safety factor, it is entirely possible that regulations could be worked out that would meet the goals of both parties. The smaller this safety factor can be made the lesser will be the distance between the two parties. Like any design situation, safety factors, although necessary, are expensive—the better the science behind the regulations, the more precise the regulation should be. It is to everyone's advantage if we carefully determine just what protection is needed for industrial sludges.

It appears that while every plant must take on the responsibility of cost-effective implementation at its site, the Government, with its research resources, also must attempt to minimize the "overkill" in its regulations, while assisting in the development of technology that can assist the manufacturers in implementation. If this is done, perhaps we can take a responsible, effective approach to the problem.

Minimizing Costs by the Manufacturer

In attempting to resolve the residue problem, the manufacturer faces a three-way trade off between the investment required for concentrating the sludge on-site, the higher hauling and final disposal costs if little or no investment is devoted to concentration, and the use of in-plant changes and selection of treatment chemicals which reduce the sludge volume generated. Minimizing the amount of sludge generated is extremely important for some situations and is being addressed by a separate paper in this session.

The trade off between the cost of concentration and the cost of hauling and disposal is an almost classic optimization problem. In many cases, however, there are other special factors that are specific to an individual site. Sludge disposal is often strongly affected by local opportunities, such as the proximity of a chemical landfill area or the availability of a contract disposal firm as well as by the economic balancing of sludge concentrating investment versus hauling costs.

The need for concentration in many cases is illustrated in Figure 1, which shows the effects of sludge concentration on the volume of sludge. The relative cost of the sludge concentration equipment, which can be used to reach these higher percent solids levels, is shown in Figure 2. If you superimpose these two figures (Figure 3) you can obtain a good feel for the basic problem in sludge disposal. To obtain low sludge volume you must remove a portion of the water associated with the sludge. This water is often expensive to remove. For the small manufacturer, the relative cost of the sludge concentrating equipment can be quite high, even if the optimum system is chosen.

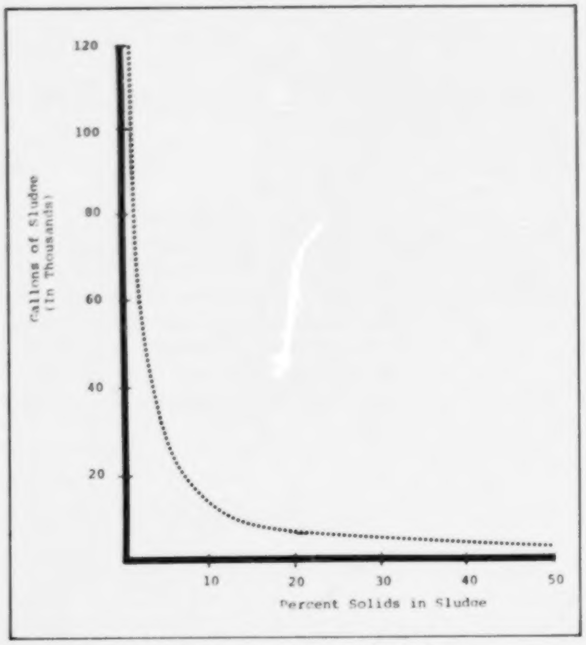

Fig. 1—Effect of Solids Concentration on Sludge Volume.

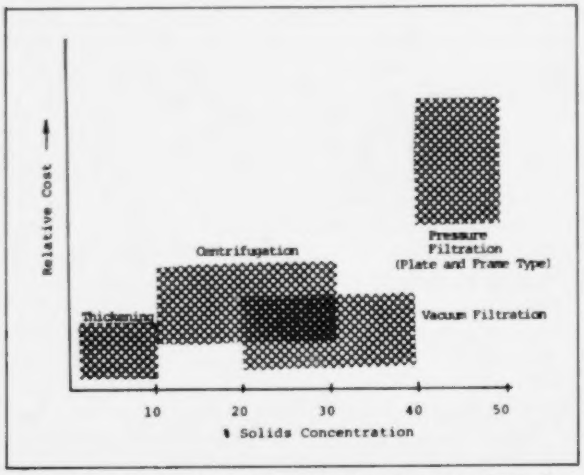

Fig. 2—Concentrations Achievable with Various Dewatering Methods.

Minimizing Regulatory Safety Factors

While the manufacturer is trying to minimize the resources required to accomplish his portion of the task, it is equally important for the regulatory agency to shoulder the burden of making the regulations as precise, specific, and cost-effective as is possible. To do this, they

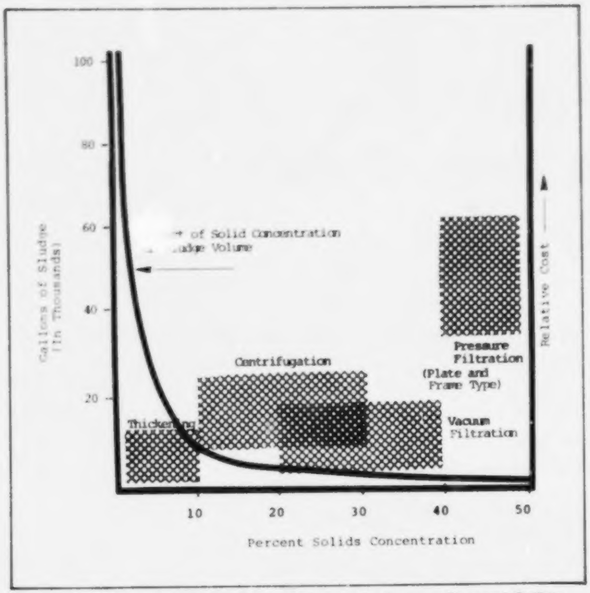

Fig. 3—Sludge Volume and Cost of Concentration vs. Percent Solids.

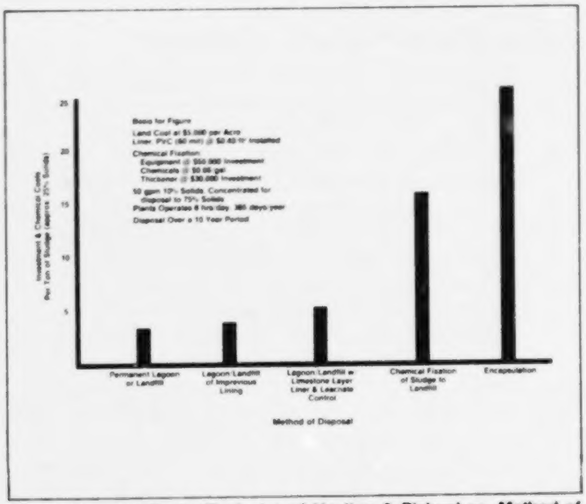

Fig. 4—Disposal Costs (Exclusive of Hauling & Pickup) vs. Method of Disposal for One Application.

need scientific and cost data. Anyone trying to derive guidelines that are to be applied nationally quickly learns that no regulation is cost-effective in every situation, but an effort must be made to minimize wasted resources. The vast amounts of funds that are to be expanded as a result of Federal and state regulations gives tremendous leverage for the expenditure of R&D funds to provide more precise regulations—regulations that serve the intended purpose but do not have excessive overkill built in. We do need research that will pinpoint the real trouble spots so that proper attention can be focused on the important areas.

The affect of the type of final disposal on cost is shown in Slide 4 for one specific case. The investment curve rises sharply as we approach the complete containment systems. We certainly want to keep these rising costs in mind, and to use the most expensive types of disposal methods only when necessary.

Summary

Summarizing then, the problem of disposing of the residues of wastewater treatment is now at hand. We need a systematic scientific approach for determining the handling of these residues. The regulation should be specific enough to prevent treating relatively safe sludges in the same manner as toxic sludges.

The regulations for disposing of sludges in a way that protects the environment must not be so imprecise as to cause a needless adverse economic impact on industry. The technology must be developed in a way that benefits both causes. The new Resource Recovery and Conservation law is not excessively restrictive if properly applied. Much more authority for enforcement is being encouraged by the States. Strict compliance is required only for hazardous wastes. The new law might require more record keeping and more care in selecting a disposal site or transporter, but most people agree that this is badly needed.

The control of the residues is important. We have spent large sums to clean the wastewater and we do not want to jeopardize this investment. On the other hand, we cannot afford to be so sloppy in our science and engineering that we waste resources. The key is to perform the research and development necessary to have an understanding of what we are doing. This session presents results on some of the efforts that are being directed toward obtaining this understanding.

Minimizing the Generation Of Metal-Containing Waste Sludges

F. A. Steward & Leslie E. Lancy*

INTRODUCTION

Chemical treatment is the backbone of all available technology for treatment of metal finishing waste waters. While there is an array of other techniques available, each has a specialized and rather limited field of application. For the foreseeable future, chemical treatment is likely to be an essential component in any complete treatment plant. Unfortunately, much of the chemical treatment technology depends on removal of noxious constituents from the waste water by precipitation as insoluble solid material, commonly referred to as sludge. Typical reactions are the precipitation of heavy metals, water hardness, fluorides, phosphates, and sulfates. The handling and ultimate disposal of these sludges is, and will continue to be, a steadily increasing cost factor for the industry. There are a number of reasons for this. Metal-containing sludges are hazardous when disposed in conventional sanitary landfills. Regulatory attention on this solid waste disposal issue will continue to grow and regulations will tighten. Approved disposal sites, operating under regulatory permit, are rare at the present time and likely to be scarce for years to come. The quantities of sludges presently generated will increase dramatically due to the requirement for pretreatment of industrial wastes prior to discharge to sanitary sewage systems. Finally, there is a tendency to meet extremely tight regulatory requirements by treating with significant excess quantities of sludge-producing materials such as iron or aluminum salts, clay, peat moss, and organic xanthate compounds.

The economics of metal recovery are steadily improving as a result of three factors. There is increasing concern over the potential environmental harm which can be created by disposal of heavy metal-containing sludges, especially when combined with sanitary solid wastes. The value of most metals is climbing due to scarcity of domestic ore reserves, increasing costs of production, etc., and finally, there is a constant advancement in the technology of metal recovery. This shifting framework justifies a continuous reevaluation of the various recovery schemes available to our industry. This paper is a review of the most significant sources of metal salt wastage, and thus sludge generation, as well as an attempt to critically evaluate some of the techniques in current practice.

Even after implementation of expected dramatic advances in recovery technology, there will be a certain level of residual waste sludge generated by typical metal finishing operations. We are strongly of the opinion that recovery from such mixed waste sludges will not be economical in the foreseeable future. Therefore, the subject of ultimate disposal techniques and associated regulations is very important for our industry. As implied by the title of this paper, methods to reduce the generation of metallic sludges will be discussed, but not the problem of dealing with the valueless mixed residues.

Sources Contributing Metal to the Sludge

The most easily recognized source of pollution in a metal finishing operation is the dragout of various processing baths into subsequent rinsing steps. It is commonly assumed that this is the main source of metals which ultimately generate waste sludge. As reported earlier[1], our investigations show that 70 - 80% of the metal content in the sludge is derived from various sources other than dragout. Examples are the dumping of process solutions, purification of various baths, backwashing of filters, and accidental spills to the floor. The basis for our conclusion is the routine design calculations which have been done for many hundreds of waste treatment plants over the twenty-five years of our company's experience. Calculations are based upon site investigations, chemical purchasing records, and dumping schedules for the various process baths. As an illustration, we find that in large nickel plating installations, more nickel is lost through the sludgery bottom dumps after chemical purification and from operation of the filters than through normal dragout. Equally significant is the zinc or cadmium that is stripped off the danglers or rack tips in the acid dip in the cleaning cycle, or removed from the work in dichromating. One outstanding exception to this rule is decorative chromium plating where the main metal loss is due to dragout.

The bulk of metal wastage in our industry is a result of copper and brass bright dipping, pickling and etching of various metals, dichromating, stripping, deburring, and tumbling.

We don't mean to imply that metal losses due to dragout are insignificant. Indeed, they can amount to 6-7% of the metal purchased by a plant. However, we feel it is

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important to counter a common misconception since an intelligent plan for minimizing the generation of metal sludges must be based on proper understanding of the sources.

Metal Recovery from Dragout

The majority of the effort to date, and thus the available technology, is focused on metal recovery from dragout. An obvious approach for those process baths which operate in a reasonably balanced or equilibrium condition, is to return the dragout directly. Since rinsing, by definition, dilutes the dragout, some means is needed to reconcentrate it prior to return. Most systems use countercurrent rinsing, and one or a combination of the unit operations of evaporation, reverse osmosis, electrodialysis, and ion exchange. There is voluminous literature available covering all of these approaches and giving detailed process descriptions, case histories, and operating cost data. It is beyond the scope of this study to consider the trade-offs among these approaches in view of the wide array of potential applications. The wealth of available published information is a more suitable source for anyone interested in the subject.

In some processing systems, return of dragout can be impractical. This is obviously the case with those processing baths which become steadily depleted in use since return of the dragout would simply increase the frequency of dumping. However, it is also true when a balanced process, such as the typical electroplating bath, might be harmed by return of contaminating materials such as trace metals, organic compounds, undesirable salts such as carbonates, etc. In these cases, recovery can still be practiced by one of two means.

1. An electrolytic cell can recover the metallic content from the dragout. A number of cells have been proposed for removal of mg/l concentrations of metals in normal rinse water flows[2]. These have relatively low current efficiency, and result in a powdery metallic deposit which requires a special handling technique to separate from the water stream, dry and melt. As an alternate, we use the integrated metal recovery approach[3,4]. A recovery-rinse liquor is circulated through a specially designed electrolytic cell and thus maintained at rather low metal concentration. Drag-out to subsequent rinses is negligible as far as chemical load sludge generation and value. Because this approach allows a good electrolyte to be maintained, the deposit is sound metal with higher resale value and the potential to be used as anode material in plating operations. The current utilization efficiency is also much higher, typically above 98%.

2. Segregated precipitation and collection of a specific metal sludge can allow recovery of its value. Such sludges are salable as chemical byproducts. Alternatively they can be dissolved in an electrolyte solution and deposited as a high-purity cathodic metal to be sold or used as anodes.

Because of increasing metal cost, the recovery of even such low-cost metals as zinc is becoming economically advantageous. Several firms have recently expressed interest in purchasing waste slurries of zinc sludge, further confirming the steady shift in the economic framework.

Metal Recovery from Processing Solutions

As stated earlier, process solutions which must be periodically discarded because of accumulation of dissolved metal constitute one of the main sources of metal-containing sludges. Unfortunately, there are so many processing solutions which are routinely discarded, each having its own particular chemical make-up, and each requiring a specific regeneration approach, that it would be impossible to discuss all of the problems and all of the potential solutions. What we would like to do is to discuss those recovery methods which we have had an opportunity to investigate, and which, in our opinion, have been successful as an economical regeneration approach.

It is also important to stress that economics invariably dictates a certain minimum size for a regeneration system. Even the simplest regeneration set-up requires investment in equipment, engineering involvement, space, labor, and maintenance. The calculations to establish the economics of any process can't be judged by the apparent low-cost chemical additions, electrical or heat energy, etc., but have to include amortization of total investment (which is usually the most significant cost item), the value and cost of the space occupied, as well as the labor and maintenance costs. Only large-volume processors who are wasting significant quantities of metal will find that the installation of these regeneration processes is economically justifiable.

1. *Copper and Brass Pickling.*

a. Electrolytic Regeneration Systems have been in use for many years now and are installed at most copper rod and wire mills[5]. Copper rod, flat sheet stock, extruded tubing, etc., leave the hot primary forming operation (unless the extrusion is performed under a protective atmosphere) with substantial scale on the surface. The scale contains both cupric and cuprous oxide which is removed by a hot sulfuric-acid-type pickling solution. The cuprous oxide is not soluble in sulfuric acid. Much of it falls off during the pickling process and accumulates as a sludge in the acid. Significant quantities are also lost in the subsequent rinsing operation, particularly when high-pressure sprays are used to dislodge it. The continuously recirculated pickling solution is pumped through an electrolytic cell where dissolved copper is plated out at near 100% cathode efficiency, using insoluble lead anodes. The copper concentration is maintained in the range of 25 - 45 grams per liter and since the pickling acid doesn't have to be discarded, as much as 60% of the dragout losses can also be recovered through the use of a simple dragout reclaim rinse.

b. Brass and the various bronze alloys pose a somewhat different problem. It has been assumed that the alloying elements interfere with deposition of metallic copper and cannot provide a smooth, heavy deposit meeting the cathode plate purity requirements. During the course of an EPA demonstration project[6], the opportunity was given to prove that cathode plate integrity and purity could be maintained, with a recovery cell operating at a lower than normal current density, even though the pickling acid contained significant concentrations of other metals such as zinc, nickel, and tin. Especially the zinc concentration will increase to high levels, but an equilibrium at these levels is eventually reached due to dragout losses with no deleterious effect on the pickling efficiency of the acid or on the cathode plate quality.

c. Basket or barrel pickling of brass pieces may also create a problem with a red coppery immersion deposit when the content of the acid exceeds 12 - 15 g/l copper metal. Traditionally, frequent dumping of the acid bath was considered the only suitable processing method. However, installation of an electrolytic recovery cell allows the copper to be maintained below 10 - 12 g/l and perpetuates the use of the bath. The use of special electrolytic recovery cells, designed to operate with high efficiency at low metal concentrations, makes these types of recovery systems feasible. Economical justification can be found for even rather small size installations.

d. When the pickling or etching bath for copper or copper alloys contains sulfuric acid and hydrogen peroxide, crystallization becomes a more cost-effective approach for regeneration[6,7]. The main purpose for developing the peroxide-containing process baths was the more thorough removal of cuprous oxide from the copper and copper alloy surfaces. The hydrogen peroxide content allows dissolution of the otherwise insoluble cuprous oxide, accelerates the pickling process, and results in an overall quality improvement for a variety of products including copper wire and sheet, beryllium copper parts, and electronic printed circuit boards[8]. The driving force provided by the peroxide allows the bath to be operated near the solubility limit of copper. Thus, the bath can be operated at slightly elevated temperature and regenerated by a simple cooling of 20-30 degrees to cause crystallization. The accumulating high-purity copper crystals can be sold or used for make-up to an electrolytic copper recovery cell. Direct electrolytic regeneration of these baths is also possible, but it increases the consumption of hydrogen peroxide and is thus less attractive.

2. *Steel Pickling Solutions*

Steel pickling solutions based on sulfuric acid are amenable to regeneration by crystallization and continuous removal of the accumulating iron content very similar to the process as described for copper cleaning. Increased pickling rate and iron solubility is gained by the operation of the pickling system at 140 - 160° F and at the same time the continuous removal of the accumulating iron content is made simple by cooling a relatively low volume of recirculated acid, dropping the temperature by 20 - 30 degrees.

This process has been in use for many years, but mainly by the primary steel manufacturers. The recovery systems were designed for the batch treatment or continuous removal of large volumes of acid and iron crystals. With the development of simple, small-scale crystallizers, this process should be attractive for the metal finishing plants in a more general sense. Sludge handling and disposal costs have markedly changed prior assumptions regarding economy, the accumulating iron crystals can be sold most often locally, since many municipal sanitary treatment plants use iron salts for tertiary treatment and sludge conditioning.

3. *Electrodialysis Systems for the Regeneration of Chromic-Acid-Based Processing Solutions*

a. Before plastic parts are plated with a metallic coating, the surface is etched to promote adhesion. The typical etch solution contains 200-400 g/l chromic acid and 20 - 30% sulfuric acid. It is very viscous, creating a thick dragout film, and resulting in dragout losses six to ten times greater than for most other metal finishing process baths. The dragout losses are not normally recovered because it is assumed that the breakdown products of the dissolved organic materials from the plastic will accumulate. Most of the processing baths are maintained by chemical additions to replenish the heavy dragout losses, thus allowing an equilibrium to be established where impurity accumulation is balanced by dragout. Electrodialysis of recovered dragout reoxidizes the trivalent chromium to the hexavalent form, greatly reducing the required chemical additions.

b. Current efficiency and the quality of the electrodeposit are both impaired in hard chromium plating if metallic contamination exceeds 8 - 10 g/l of iron or 10 - 12 g/l of copper. The hard chrome baths gain in these impurities at a rate which depends on the type of parts handled and the etching process used before plating. Usually dragout losses are very low, so that bath must be purposely wasted to maintain the desired equilibrium. After many years of development work which has been hampered by the low iron and copper limits which must be maintained, we feel that electrodialysis has the potential to eliminate purposeful wastage of the plating bath[9]. This is particularly significant since the sludge generation is disproportionately high for the low levels of metallic contamination due to the chromic acid concentration in the plating bath.

4. *Zinc Phosphate Solution Maintenance by Gravity Settling*

Phosphating solutions generate an iron phosphate precipitate during operation. The precipitated iron phosphate tends to clump together and accumulate as a heavy sludge on the bottom of the tank, or as a scale on the heat exchanger coils. Continuous recirculation of the solution from the processing tank to a settling tank avoids the accumulation of sludge or scale by providing favorable conditions for the iron precipitates to agglomerate and settle in the auxiliary vessel. The need for periodically dumping the processing solution to be able to clean out the tank or the heat exchangers can be eliminated, and the life of the processing solution perpetuated.

5. *Electrolytic Maintenance of Chelated Scale and Smut Removal Baths*

In many plants, highly-stressed steel parts are cleaned after heat treatment with an electrolytic cleaning bath containing high concentrations of chelating agents, and sometimes also cyanide. The process deteriorates rapidly as the iron content increases. Continuous, low-current-density electrolytic iron removal is feasible, and can be accomplished without large losses in cyanide content, thus extending the life of the process bath several times over normal expectancy[10].

6. *Recovery of Nitric Acid and Molybdenum in Light Bulb Manufacturing*

In manufacturing incandescent light bulbs, tungsten filaments are wound around a molybdenum tube mandril. After heat treatment of the filament, the molybdenum tube is dissolved in nitric/sulfuric acid, leaving the wound filament behind. Removal of molybdenum by precipitation cannot be accomplished except with high ratios of iron addition to form an iron molybdate coprecipitation product. The recovery of molybdenum from this sludge is impaired by the reduced value of the mixed metallic sludge.

Distilling off the nitric acid from the nitric-sulfuric acid dissolution bath allows recovery of nitric acid at a sufficient concentration to be used in the make-up of a new bath. The sulfuric acid remaining after distillation is highly concentrated and contains a sludgey precipitate of molybdenum tri-oxide. After solid-liquid separation, the sulfuric acid can be reused in reconstituting a new bath by combination with the nitric acid distillate. The pure molybdenum oxide is sold to a refiner and ultimately recycled to the manufacturer of the molybdenum tubing.

7. *Recovery of Metals from Stripping Solutions*

There are many large-scale industrial recovery systems in operation for the purpose of metal recovery from waste materials, purification of scrap, etc. A number of them are mentioned here to indicate the variety of processing methods that are available.

a. Tin is stripped from metal can scrap with a caustic soda solution. The tin is recovered by crystallization of sodium stannate or electrolytically recovered as the metal.

b. We have developed a stripping process[11] for copper wire scrap, removing the tin with a sulfuric acid-copper sulfate strip solution, and precipitating the tin oxide in a purity suitable for the metal refinery. The copper scrap requires only remelting to prepare ingots for rolling into wire rod.

c. Cyanide-type silver stripping solutions can be operated with a continuous electrolytic recovery system that provides a salable silver foil.

d. A cyanide-type nickel strip solution allows the simultaneous recovery of a low-purity cathode deposit of nickel, while the cyanide content of the spent strip solution is economically oxidized.

e. Electrolytic nickel stripping solutions of sulfate or nitrate basis can be operated at saturation level insofar as nickel concentration is concerned. The nickel, as it is solubilized at the anode, becomes insoluble in the solution and precipitates as nickel oxide. These types of solution do not require dumping and the nickel oxide can be removed as a heavy sludge from the stripping system[12].

f. Cadmium can be recovered at sufficient purity from an ammonium nitrate type stripping solution by cementation on aluminum powder. The recovered sponge is sold to the refinery.

The examples are enumerated mainly to show the varied technology that is available and could be potentially considered for the particular process at hand. It is hoped that the chemical suppliers of the various stripping process solutions will provide metal recovery recommendations for their particular process. It can be postulated that if such concern and interest is evidenced by the industry, competition between the suppliers will automatically channel future developments in this direction.

8. *Metal Recovery from Sludges*

Segregated metal sludges lend themselves to the installation of simple and economical metal recovery systems. Experience along these lines has been gained over many years in working with the integrated treatment approach which allows segregated collection of the various metal sludges.

a. Plating solution losses due to filtration and batch purification operations are significant. The main purpose of purification and filtration is the removal of organic contaminants (breakdown products of the various brighteners, leveling and wetting agents, etc.). An additional interest may be the removal of accumulating iron or other metallic impurities, or of suspended dust particles which are removed in the filtration process. In nickel plating systems, we have found that the losses due to purification and filtration may exceed the losses through dragout. The sludgey remains after batch purification may amount to a solution layer of 6-8″ on the bottom of the treatment tank. Attempts to reduce the volume of this layer cause clogging of the filter which is used to return the solution to the plating tank. Filters should be drained before blowing down the accumulated cake, but even under these conditions, significant losses occur when the filter media is hosed off before a new filter is built up again. These combined wastes can be neutralized, the metal precipitated as the carbonate or hydroxide, and the accumulated sludges collected, washed and reprocessed for recovery. During the washing stage, the soluble salts and organics are removed. The sludge contains the precipitated metal and insolubles such as carbon filter aid and metallic fines.

Metal recovery from the sludge can be accomplished either through dissolution by a recirculated electrolyte, that is depleted of metal in an electrolytic cell with a simultaneous decrease in pH (generation of acid). The dissolution of the metal hydroxide (or carbonate) reestablishes the working pH and the metal content.

A second approach is through dissolution of the sludge with a heated, dilute acid solution. The free acid is neutralized by the metal that is going into solution. The re-dissolution is very rapid if the metal hydroxide sludge has not been allowed to dry out and therefore dehydrate[13]. As an example, with nickel sludge, the free acid is neutralized to a pH of 3.6-4.0. A dilute acid solution is made up to provide a saturated nickel sulfate or nickel chloride solution at room temperature and is recirculated through the sludge until the desired final pH has been reached. Possible iron contamination can be precipitated with hydrogen peroxide additions and filtration together with the insoluble carbon, filter aid, etc. An EPA-sponsored demonstration project is in the planning stages, and it is hoped that both quantitative and qualitative data, together with accumulated information on operating costs, will provide the desired background as educational input for a process such as this for the industry at large[14].

b. In aluminum anodizing, caustic soda etching, or aluminum milling processes, significant quantities of aluminum are dissolved and ultimately discharged as sludge. If such aluminum-containing baths are kept segregated from the chromate and smut removal acid baths (deoxidizers) which are likely in such a plan, the resultant sludge can be of sufficiently high purity to generate a salable byproduct. Trace metallic contaminants such as iron, zinc, and magnesium are at low enough concentrations to be acceptable. Assuming that the sludges have been segregated, and that calcium has been used for neutralization, the sludge can be dissolved in a waste sulfuric anodize solution, which has been supplemented by additional sulfuric acid so as to result in an aluminum sulfate solution which is at or close to saturation at room temperature. This aluminum sulfate concentrate is readily salable as a coagulant for sewage treatment or for waste water treatment in pulp and paper or other industrial operations requiring alum additions.

Summary and Conclusions

There are many techniques available to reduce the quantity of metal converted to waste sludge. A thorough trade-off analysis is needed to select the best candidate for each specific application.

For recovery from rinse waters, return of drag-out, electrolytic methods or segregated collection of a salable sludge are demonstrated.

Discarded process baths represent the largest source of metal sludge generation. Electrolytic deposition, crystallization, precipitation/sedimentation, electrodialysis, and cementation have all been demonstrated as practical techniques for regeneration of process baths, allowing recovery of metal values, reduced treatment chemical consumption and reduced discharge of soluble salts.

Further progress will be accelerated as the finishing industry presses its chemical suppliers for process bath formulations more suited to such regeneration methods.

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Research on Impoundment Materials

Robert E. Landreth*

INTRODUCTION

Low permeability materials have been utilized to seal water impoundments and as canal linings for decades. Their function is to minimize the loss of water by seepage. Most of these applications have been very successful and are still in use today. However, our highly technological and urban society has presented us with a new problem. Vast quantities of industrial and solid wastes are being disposed of or stored on the land. These disposal and storage sites, unless properly constructed, have a potential for pollution of ground and surface waters by the leachate generated by the wastes. The availability of naturally occuring acceptable disposal sites is decreasing because of environmental and economic impact. Therefore, the use of artificial liners will most likely increase in order to minimize the environmental stress and to utilize those sites not acceptable without lining. The use of artificial liners will necessitate additional site design. Since liners are part of a leachate collection system provisions must be made to remove the leachate and disposed of in an acceptable manner, e.g., treatment, recirculation, discharge to sanitary sewer, etc. The question being asked now is which type of liner to use and how long it will last. The Solid and Hazardous Waste Research Division, Municipal Environmental Research Laboratory, U. S. Environmental Protection Agency is attempting to answer these questions via a series of research contracts.

Due to the variety of waste streams and the differences in liner materials the research approach is to develop meaningful test data so that the user community can determine liner compatibility as relates to leachate attack.

Four research projects have been initiated to develop a data base from which evaluation criteria or test protocol can be established.

State-of-the-Art

A literature search and state-of-the-art survey of those liner materials being utilized for containment of seven general types of industrial wastes has been completed (1). The objective of this study was to assemble data associated primarily on chemical interactions of waste and potential liner materials. Physical properties, cost and field performance data were also collected for various membrane types. Potential liner materials considered were those listed below:

Polymeric membranes

- Polyvinyl chloride (PVC)
- Polyethylene (PE)
- Polypropylene
- Butyl rubber
- Chlorinated polyethylene (CPE)
- Ethylene propylene diene monomer (EPDM)
- Chlorosulfonated polyethylene (Hypalon)
- Neoprene

Admixed Materials

- Asphalt concrete
- Soil cement
- Soil asphalt
- Asphalt emulsion on non-woven fabric (petromat)

Soil Sealants

- Rubber latex
- Bituminous seal coat

Natural Soil Systems

- Soil Bentonite
- Compacted clays

The generic names, applied to the polymeric membranes, may be further subdivided based on formulations. The manufacturers can produce liner materials better suited for specific applications by adding various ingredients such as plasticers, resins, fungicides, biocides, fillers, etc. These added ingredients also influence the cost and more specifically the physical and chemical properties of the final product. No attempt was made to identify specific formulations or to subdivide the broad general classification. The intent of this project was to give guidance on which liner materials to consider from a waste compatibility standpoint and not to specifically identify liner performance.

The waste streams considered for containment by these liners were:

- Caustic petroleum sludge
- Acidic steel-pickling waste
- Heavy-metal-bearing electroplating sludge
- Toxic pesticide-formulation waste
- Oily refinery sludge
- Toxic pharmaceutical waste
- Wastes from rubber and plastics industries

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Waste streams were selected based on general industry studies. The characteristics of these wastes are described in detail elsewhere (1). In general, these wastes streams contained wide ranges of biochemical oxygen demand (BOD_5), (TOC), and total suspended solids (TSS). The data that were available on the waste chemical characteristics formed the basis for selecting the liner material(s) most suited to contain the waste for a given situation.

Through the course of the literature review and discussions with manufacturers, fabricators, suppliers, installers and trade association representatives a matrix of data was developed on liner-waste compatibility. This matrix data is presented in Table 1 which is only to be used as a guide. However, the final liner material selection is more complicated and requires additional factors for consideration. For instance the liner material formulations may be changed to upgrade their performance for a particular waste stream or to change a physical property such as tensile or color. The sludge/waste identified in the table may not be chemically similar to the one in question and additional compatibility test may have to be performed. The site conditions and many placement parameters must also be considered before a best final selection can be made. However, the table is functional since it will eliminate from consideration those materials that are not compatible to the waste stream being considered.

Liners Exposed to Municipal Solid Waste Leachate

Three years ago a project was undertaken to assess the status of technology regarding liner materials for sanitary landfills. The objectives of this study were; to determine the effects of landfill leachate on the physical properties of a variety of polymeric membranes and admixed materials; to develop data in predicting the life of the liner materials exposed to leachate; and to develop economic data on the liner materials and associated construction costs. The initial project was to have exposure periods of 12 and 24 months. Those polymeric (flexible) and admixed liner materials considered are listed below:

Polymeric membranes

- Polyvinyl chloride (PVC)
- Polyethylene (PE)
- Butyl rubber
- Chlorinated polyethylene (CPE)
- Ethylene propylene diene monomer (EPDM)
- Chlorosulfonated polyethylene (Hypalon)

Admixed materials

- Hydraulic asphalt concrete
- Paving asphalt concrete

COMPATIBILITY OF LINER MATERIALS WITH VARIOUS INDUSTRIAL WASTES

Name of liner	*Short name*	*Vulcanized*	*Caustic petroleum sludge*	*Acidic steel pickling waste*	*Electroplating sludge*	*Toxic pesticide formulation waste*	*Oil refinery sludge*	*Toxic pharmaceutical waste*	*Waste water from rubber and plastics industry*
Polymeric Membranes									
Butyl rubber	IIR	Yes	Yes	Yes	Yes	?	No	?	?
Chlorinated polyethylene	CPE	No	Yes	?	?	?	No	?	?
Chlorosulfonated polyethylene	CSM Hypalon	No	Yes	Yes	Yes	?	No	?	Yes
Elasticized polyolefin	3110	No	?	?	Yes	Yes	?	Yes	Yes
Etnylene propylene rubber	EPDM	Yes	Yes	Yes	Yes	?	No	?	Yes
Neoprene rubber	CR	Yes	Yes	?	?	?	?	?	Yes
Polyethylene	PE	No	Yes	?	Yes	Yes	Yes	Yes	Yes
Polypropylene	PP	No	Yes	?	Yes	Yes	Yes	Yes	Yes
Polyvinyl chloride	PVC	No	?	?	?	Yes	Yes	Yes	Yes
Admix Materials									
Asphalt concrete - hydraulic	HAC	-	Yes	No	No	?	No	?	?
Asphalt membrane	-	-	?	?	?	?	No	?	?
Soil asphalt	-	-	?	No	No	?	No	?	No
Soil cement	-	-	Yes	No	?	?	Yes	?	Yes
Compacted clay	-	-	No	No	No	?	Yes	?	Yes
Treated bentonite	-	-	No	No	No	?	Yes	?	Yes

Chemical compatibility of lining materials with various industrial wastes. Indicates the potential suitability of a given type of lining material for confining types of wastes. For a given type of lining material compositions vary considerably as do the composition and concentration of the waste and environmental conditions under which they would be confined.

"Yes" = Lining material is probably suitable for confining a wide range of wastes of the type indicated, using a wide range of formulations.

"?" = Questionable. Suitability depends on the specific waste and the specific liner material. Immersion tests should be run.

"No" = The lining material would *not* or *probably not* be suitable for confining the type of waste shown.

See attached.

- Soil asphalt
- Soil cement

The test specimen of polymeric materials were commercially available and contained a seam either made by the supplier or a seam made in accordance with the manufacturer's recommendation. The test specimen of admixed materials were formed-in-place in accordance with the recommended procedure. In addition, 42 other polymeric liner specimens were placed in the exposure cells. These materials represented duplicate generic types of liner materials but from different manufacturers, reppresenting different formulations and thicknesses.

The liner materials were mounted at the base of simulated landfill cell lysimeters to better duplicate field conditions and allow for microbial action. Shredded municipal refuse was placed in the lysimeters and water was added on a regular basis to generate the leachate. A measured amount of water was added on a scheduled basis to maintain the quality of leachate which was consistant throughout the lysimeter cells and was "typical" of that found in actual landfills.

Results of the first 12-month's exposure produced only minor changes on the physical properties of the liner materials (2). With the exception of polyethylene and ethylene propylene diene monomer, all liner material had small losses in tensile strength. The elongation at the break increased in all cases; the modulus or stiffness generally decreased except for polyethylene, ethylene propylene diene monomer and Butyl rubber in which case it remained essentially unchanged. The heat sealed seam retained their strength the best while some major losses were observed in other seaming techniques. In all cases, the liner material softened. None of the polymeric materials allowed leachate to pass during the first year of exposure although leakage was observed through the soil asphalt concrete liner materials.

One indication of liner material permeability is the absorption of leachate by the liner material. Absorption for both water and leachate was determined. The results indicated that absorption was a function of the dissolved solids content of the leachate, both inorganic and organic. A similar swelling was observed for both water and leachate immersion in those liner materials characterized as having a high hydrocarbon structure. In chlorinated materials such as chlorinated polyethylene, chlorsulfonated polyethylene and neoprene, a substantial amount of water absorption was observed. Polyvinyl chloride had a relative low value for water absorption but a significant value for landfill leachate.

In view of the relatively small changes to the liner materials after 12-months exposure it was decided to extend the 24-month exposure period to 42 months. It is hoped that this will provide sufficient changes to establish long-term trends to predict the service life of the materials.

Liners Exposed to Industrial Hazardous Sludge Leachates

Increased concern over the pollution potential of industrial wastes has resulted in a project of exposing liner materials to industrial wastes. This study will also provide more detail to the liner-waste compatibility matrix as presented in Table I.

The objectives of this study are: to determine the effects of selected liner materials by exposing them to a variety of industrial wastes over an extended period of time; to estimate the effective life of the liner materials; to determine the cost effectiveness of liner materials; and to develop a test protocol for user community acceptance. The project was to have 12 and 24-month exposure periods. Those liner materials considered for this project are listed below:

Polymeric Membranes

- Polyvinyl chloride (PVC)
- Butyl rubber
- Chlorinated polyethylene (CPE)
- Ethylene propylene diene monomer (EPDM)
- Chlorosulfonated polyethylene (Hypalan)
- Neoprene
- Elasticized polyolefin (3110)
- Polyester elastomer (experimental)

Admixed

- Hydraulic asphalt concrete
- Soil cement with and without surface seal
- Asphalt emulsion on nonwoven fabric (petromat)
- Modified bentonite and sand
- Compacted native fine-grade soil

As with the municipal solid waste leachate study, the polymeric material test specimens were commercially available samples which contained factory supplied seams or seams which were made in accordance with recommended procedures. The admixed material test specimens were formed in place according to recommended procedures. Larger liner material specimens (4 feet square) were draped in open tanks with sloping sides. These large specimens are being exposed to attack from both the weather and selected waste leachates. A very critical area in a lined waste pond was the waste/air interface and specifically the folds in the membrane that could occur at this interface. The test tanks with sloping side walls were designed specifically to investigate this problem. A more detailed description of the experimental set-up has been published (3). In addition to the primary exposure cells, small liner material specimens (6" × 6") were placed on racks located outdoors for exposure to the elements.

Waste samples were obtained from actual industrial wastes streams. The general classes of waste are:

- Strong acid
- Strong base
- Wastes of saturated and unsaturated oils
- Lead wastes from gasoline tanks
- Oil refinery tank bottom waste (aromatic oil)
- Pesticide waste

DESCRIPTION OF INDUSTRIAL WASTE STREAMS

Caustic Petroleum Sludge

Form of waste: Aqueous solution, wash water, spent caustic.

Industrial source: Petroleum refineries, from 5.7 wt. % caustic solutions.

Process operations: Used in washing, sweetening, neutralization, hydrofining, hydrocracking, hydrosaturator, LTG treating, etc.

Composition: Wastes are 6.2 - 7.2% solids, of which 40 - 50% is caustic.

Pollutants: NaOH, salts.

Components aggressive to linings: Water, high pH, and high ion concentration.

Oil Refinery Sludge

Form of waste: Oily solids consisting of fine particles generally suspended in aqueous streams.

Industrial source: Petroleum refineries.

Process operations: Sludge from clarified once-through cooling water, exchange bundle clearing sludge, slop oil emulsion solids, cooling tower sludge, APR/Primary clarifier - separator bottom, dissolved air flotation float, kerosene filter clays, lube oil filter clays, waste biosludge, coke fines, silt from storm water run off, leaded tank bottoms, nonleaded product tank bottoms, neutralized HF alkylation sludge (CAF2), crude tank bottoms, spent lime from boiler feedwater treatment, fluid catalytic cracker catalyst fines.

Composition: Oil, water, sand and silt plus some heavy metals, organics, and corrosion-erosion products resulting from factory operations; range of oil content: less than 1 to 82 wt.%

Pollutants: Heavy metals, phenols, cyanide.

Components aggressive to linings: Water, oils, organic chemicals, ions.

Acidic Steel Pickling Wastes

Form of waste: Acidic aqueous solutions from pickling lines, pickling line scrubber discharge and pickler tank overflow.

Industrial source: Steel.

Process operations: Steel milling to remove scale.

Composition: Low pH, 1.6 - 3.1; total solids, 400,000 parts from the tank overflow.

Pollutants: Low pH and high iron in water soluble form.

Components aggressive to linings: Water, low pH.

Heavy Metal-Bearing Electroplating Sludge

Form of waste: Primarily aqueous metal salt solutions, but also sludges, filter cokes, and regenerants from ion exchange.

Industrial source: Plating industry that applied electrical coatings on surfaces by electrodeposition.

Process operations: Electrodeposition.

Composition: Chromium-bearing wastes, which include chromium, nickel, and copper, and two cyanide-bearing wastes, which include cyanide, copper, zinc and cadmium.

Pollutants: Chromium, nickel, copper, cyanide, zinc, and cadmium.

Components aggressive to linings: Water, high ion concentration.

Toxic Pesticide Formulation Waste

Form of waste: Aqueous base containing suspended and dissolved solids, e.g. clay.

Industrial source: Pesticide manufacture.

Process operations: Wash water from equipment clean-up, including filling equipment, liquid formulation lines, pumping systems, scales, spills, drum washing, air pollution control devices.

Composition: Pesticides, inerts, such as clay, and dissolved organics.

Pollutants: Pesticides.

Components aggressive to linings: Water and dissolved organics.

Toxic Pharmaceutical Waste

Form of waste: Mostly wash water from product washings, extraction and concentration by-products, and equipment wash-down.

Industrial source: Pharmaceutical.

Process operations: Chemical synthesis and fermentation processes, formulation processes, and research.

Composition: These wastes are characterized generally by biochemical oxygen demand, chemical oxygen demand, total suspended solids, and solids.

Pollutants: Many metals, cyanide, and anti-bacterial constituents.

Waste Water From Rubber and Plastics Industry (Not Solid Wastes)

Form of waste: Aqueous solutions with some suspended solids.

Industrial source:

Plastics industry: Producers of epoxies, melamines, ureas, and phenolics.

Rubber industry: Tire and tube industry and the synthetic rubber industry.

Process operations:

Plastics industry: Process waste streams.

Rubber industry: Solutions from the manufacturing processes; wash down of processing areas; run-off from raw material storage areas; spills and leakages of cooling water; steam and processing solutions, and organic solvents and lubricating oils.

Composition:

Plastics industry: Alkalinity, oils and greases, numerous organic chemicals in aqeous solutions.

Rubber industry: Waste water containing oils, suspended solids at various pH's and dissolved organics.

Pollutants:

Plastics industry: Many heavy metals and organic chemicals.

Rubber industry: Oil, grease, dissolved solids, and solvents.

Components aggressive to linings: Water, oils, dissolved organic solvents and chemicals, and metal ions.

A limited bench-scale study was conducted prior to loading of the long-term exposure cells. This study was used to screen out those liner/waste combinations that would most likely fail during the long-term exposure periods. The study did produce results that were beneficial. For example, it was found that oily wastes could not be safely contained with asphalt liners, oil wastes with aromatic components may present problems for polymeric membranes except whose membranes that are crystalline. It was also found that bentonite liners, polymer modified bentonite and soils may not be suitable for containing strong wastes containing both an aqueous phase and an oily phase. These waste streams may present a special problem because of the need of the liner material to resist simultaneously two fluids which are inherently different in their chemical reaction with the liner materials. The bench study not only produced preliminary results of liner/waste compatibility, but indicated the need for preliminary exposure tests prior to initiating long-term testing.

The results of the first year's exposure are not available at the writing of this paper. These results should be available early in calendar year 1978.

Liner Materials Exposed to Flue Gas Cleaning Sludges

A program was initiated to investigate the chemical reactivity of various liner materials exposed to wastes from the power industry. The project objectives were to determine the compatibility of the wastes with polymeric, admixed and sprayed on liner materials; to determine the effective life of the liner materials; and to obtain economic data on materials, placement and construction. The project had exposure periods of 12 and 24-months. Those materials selected for inclusion in this study are listed below:

Polymeric Membranes

- Elasticized polyolefin (3110)
- Neoprene coated nylon

Admixed Materials

- Cement Type I
- Hydrated lime
- Cement with lime
- Polymer benonite blend
- Guartec (UF) (organic filter for food preparation)
- Paving asphalt concrete
- TACSS (several different component mixes) (petroleum type product)

Sprayed-on

- Polyvinyl acetate (2 types)
- Natural rubber latex (2 types)
- Asphalt cement
- Molten sulfur

These materials are commercially available and were placed in the test cells in accordance with the manufacturer's recommended procedures.

The waste streams utilized were the flue gas cleaning sludges from coal fired power plants using lime and limestone scrubbing systems. To simulate actual field disposal situations, the exposure test cells were pressurized to 20 psi to represent a static head of 30 feet of waste sludge. The pressure was applied in increments of 2 psi per month for a period of 10 months.

The test cell construction data and first 12-month exposured data are now being assembled. These results should be available in early 1978.

Survey of In-Place Liner Materials

Field verification studies for determining liner material performance requires a substantial input of research dollars and time in order to obtain a long-term base. The ideal field verification study should include 20 liner materials; 20 waste streams; exposure periods up to 5 years; and be located at 4 different geographic locations. Since this type of study is not feasible, based on a limited budget and time constraints, an alternative study has been selected. The approach to this study is to conduct a survey to identify disposal sites where liner materials have been installed. The survey would obtain information relating to waste type, waste depth, waste age, type of liner material, owner, installer and other pertinent data on the disposal site. These data are being evaluated to determine if samples of liner materials could be obtained intack from sites of varying ages, then a long-term field exposure data base for liner performance could be developed in a relatively short period of time with minimal dollars.

The results (5) of the liner material survey were separated into municipal solid waste disposal sites and selected industrial surface impoundments. Sixty-one municipal solid waste disposal sites were identified. Of these sites, 34 used clay soil as a liner when it was installed and compacted at the base or perimeter of the disposal site. Sixteen sites used polyvinylchloride as a liner material and eight sites used asphaltic type material, either sprayed or rolled, as a liner material. The remaining three sites used ethylene propylene diene monomer, chlorinated polyethylene and butyl rubber.

Only a limited number of industrial waste disposal sites were surveyed. A wide variety of liner materials consisting of chlorosulfonated polyethylene (Hypalon), neoprene, chlorinated polyethylene, polyethylene, concrete, clay and asphalt were being utilized. At most sites, the waste composition could only be classified in broad general terms. Chlorosulfonated polyethylene (Hypalon) was the most commonly used liner material of those industrial sites surveyed. Hypalon has been used at liquid and semi-liquid waste disposal sites for the pulp and paper industry and for organic and inorganic wastes, PVC resins and latex, coal and other power plant wastes, alkaline waste, acid-iron sulfate waste, oil and waste water, battery manufacturing waste and fertilizer waste water. Polyvinyl chloride (PVC) has been used as a liner material by the fertilizer industry to contain lime and fluoride waste and as a general chemical waste pond lining. Ethylene propylene diene monomer (EPDM) has been used for acid wastes, organic wastes, mercury cell production waste and power plant waste.

One disposal site containing fertilizer waste used hypalon on the sides and PVC on the bottom. This combination offered economy as well as resistance to weathering at the air/liquid interface. It may also present some problems at the Hypalon/PVC interface as seaming or joining the two materials may present problems.

Future Activities

The need for information and data on the successful methods for site preparation and actual liner placement is becoming more apparent. Known failures with pond linings can be traced to poor liner selection, improper site design, and placement of the liner under adverse weather conditions. The research results to date strongly suggest the need for waste-liner compatibility testing before the final liner selection. However, the fact that the liner and waste are compatible only solves half the problem. The design must take site factors into account before the job can be completed. As a minimum the liner design should be based on the following information.

- Waste type and characterization to include pH; temperature (inlet); flow rate; % solids; aeration requirements; and particle size of solids.
- Job site location including temperature both high and low; wind velocity; potential for hail (with size); proximity of groundwater; type of soil at site (% sand, % clay, % silt); amount of traffic and type; access to site by animals (with type); vegetation.
- Pond requirements including size (length, width, depth and ratio); degree of compaction on the insitu soils; number of inlets or outlets with size; type of vegetation; must liner be attached to concrete; number, size, and type of stanchions. It would be very desirable to include a sketch of the pond especially if it is irregular in shape.
- Time requirements such as bid date including bid specification, type of installer preferred; time allotted for installation, labor requirements (union, non-union, plant including pay rates); proposed installation date.
- Payment including terms of contract and delivery.
- End user and design and construction engineering firm (with location and contact numbers).

With the above information a reasonably good selection of liner materials can be made. A bench-scale test, using the actual waste with the candidate liner materials will increase chances for success but may not necessarily guarantee it. These bench scale tests should include samples of both factory and field seams. The physical properties of the candidate liner materials should be reviewed before and after exposure to determine any detrimental changes associated with leachate attack.

When all the above information is obtained and more then one liner material is considered acceptable then the economics should probably dictate final selection. Too many times we consider the economics first without regard to the technical aspects which results in poor performance of liner materials.

Summary

There are liner materials currently available which can minimize the potential for groundwater pollution from landfill leachates. As the requirements for containment of more complex waste streams increase, new liner materials will need to be developed to meet those requirements. The long-term effectiveness of liner materials to contain a variety of waste streams will depend upon the correct selection of liner materials, the use of good engineering practice in the design, construction and placement of the liner materials, and the operation of the landfill site.

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Control of Pollution from Leachates

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ABSTRACT

A laboratory evaluation of the natural sorbents, vermiculite, illite, kaolinite, acidic and basic fly ashes, and zeolite is presented for the removal of cations, anions and organics under flowing conditions from an acidic petroleum sludge leachate, a neutral calcium fluoride sludge leachate, and an alkaline metal finishing sludge leachate. Activated alumina and activated carbon are involved in this study for comparison purposes since these materials are commonly used for the treatment of industrial waste streams.

The results indicate that rather than a single sorbent, a combination of acidic and basic sorbents (which induce acidic and alkaline conditions repectively into the leachate) is required in a layered system for the removal of all the measurable contaminants present in the leachates. These are illite, vermiculite and zeolite for the acidic leachate, illite, acidic fly ash and zeolite for the neutral leachate and illite, kaolinite and zeolite for the alkaline leachate based upon a comparison of their sorbent capacity (total amount of specific cations, anions or organics removed by a gram of each sorbent). The sorbent capacities exhibited by the natural sorbents for the removal of the cations, anions and organics in the leachates are comparable to those exhibited by the refined sorbents.

pH control of the leachates by combined use of the acidic and basic sorbents is essential for effective treatment. The removal of the anions in the leachates are favored by acidic conditions, the cations by basic conditions and the organics either by acidic or basic conditions.

The effectiveness of the sorbents in treating a desired volume of leachate is shown to be dependent upon the leachate velocity through sorbents and sorbent capacity. The leachate velocity defines the extent of removal of specific contaminant by the sorbent. The sorbent capacity whose magnitude is influenced by pH and concentrations of contaminants in the leachate defines the amount of sorbent required.

INTRODUCTION

The purpose of most waste treatment processes is to convert the pollutants into a gas, such as carbon dioxide, or into a solid which can be readily removed from the waste streams. In the latter instance, the end product is a sludge which must be disposed of in an environmentally acceptable manner. At the present time, ocean dumping and landfills are two methods being utilized for the disposal of this sludge. However, ocean dumping is to be banned by congressional action in 1981; thus, landfills will be the remaining receptacle for these sludges.

The disposal of sludges in landfills can lead to heavy metal, toxic anions and organic contamination of surface- and groundwaters from leachate which results from groundwater seepage or rainwater filtration through these sludges. In general, this contamination can be minimized by one of the following treatments:

a) *Chemical fixation of the sludge* (to prevent contamination of the leachate). This method applies physico-chemical principles to fix, or stabilize, the contaminants in the sludge so that they would not leach to its environment. While the concept of this approach is most desirable, it is expensive and leads to a significant increase in the volume of material that must be disposed of.

b) *Selective location of landfill site.* In this method the landfill is located at adequate distances from surface or groundwater so that the natural clay components in the soil will attenuate the pollutants in the leachate. The cost of this method may be the most inexpensive in certain cases, but adequate sites are becoming scarce.

c) *Lining the landfill site.* This method consists of lining the landfill with an impermeable membrane thereby collecting the leachate resulting from rainwater filtration through the sludge, then treating it with conventional physical-chemical methods such as activated carbon and alumina. While this approach is widely used, it is expensive because the cost of these refined sorbents require regeneration facilities. This expense can be overcome if inexpensive sorbents such as clays in combination with fly ash can be used to treat the leachate.

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The latter treatment method, in essence, simulates what mother nature does but in a controlled manner. Further, it is appropriate for sandy areas where little attenuation of the contaminants in the leachate can be achieved.

This investigation has been concerned with the latter treatment. It consists of (1) defining the clay-fly ash combinations which are most effective in removing the heavy metals, toxic anions, and organics present in leachates originating from industrial sludges, (2) examining the effect of such factors as pH of the leachate and velocity of leachate through the sorbent in removing the contaminants, and (3) establishing a design approach for this treatment.

The sludges used in this study were a calcium fluoride sludge of the type generated by the electronics and aircraft industries, a metal finishing sludge, and a petroleum sludge. These sludges were selected because their annual production is of significant magnitude to present disposal problems. The leachate from these sludges exhibited pHs that were neutral, basic and acidic, respectively. Also, it was anticipated that their leachates would contain a cross section of heavy metal hydroxides, anions such as cyanide and fluoride, and organics.

The sorbents selected for this study were acidic and basic fly ashes, vermiculite, illite, kaolinite, and zeolite (natural). The refined sorbents, activated alumina and activated carbon, which are presently used for the removal of cations, anions and organics in industrial waste streams were included in this study for comparison purposes.

EXPERIMENTAL

The preparation of the industrial sludge leachates and the analytical procedures utilized in this study are discussed in the final report (1) submitted to EPA covering the first phase of this study.

Laboratory Lysimeter Studies

Laboratory lysimeter studies were conducted using 500 g of each sorbent material. Since "pure" clay lysimeters did not exhibit adequate permeability characteristics, illite, kaolinite, vermiculite and zeolite were prepared as a mixture consisting of 80 percent inert Ottawa sand and 20 percent clay. This ration was arrived at after a series of studies established that this would permit adequate flows of leachate through these sorbents.

Lysimeters used in the laboratory were constructed of plexiglass tubing (6.2 cm i.d.; 0.6 cm wall thickness; 90 cm length), supported in a vertical position. The laboratory arrangement of the lysimeters are shown in Figure 1. A 164 micron pore size corundum disc (6.10 cm diameter;

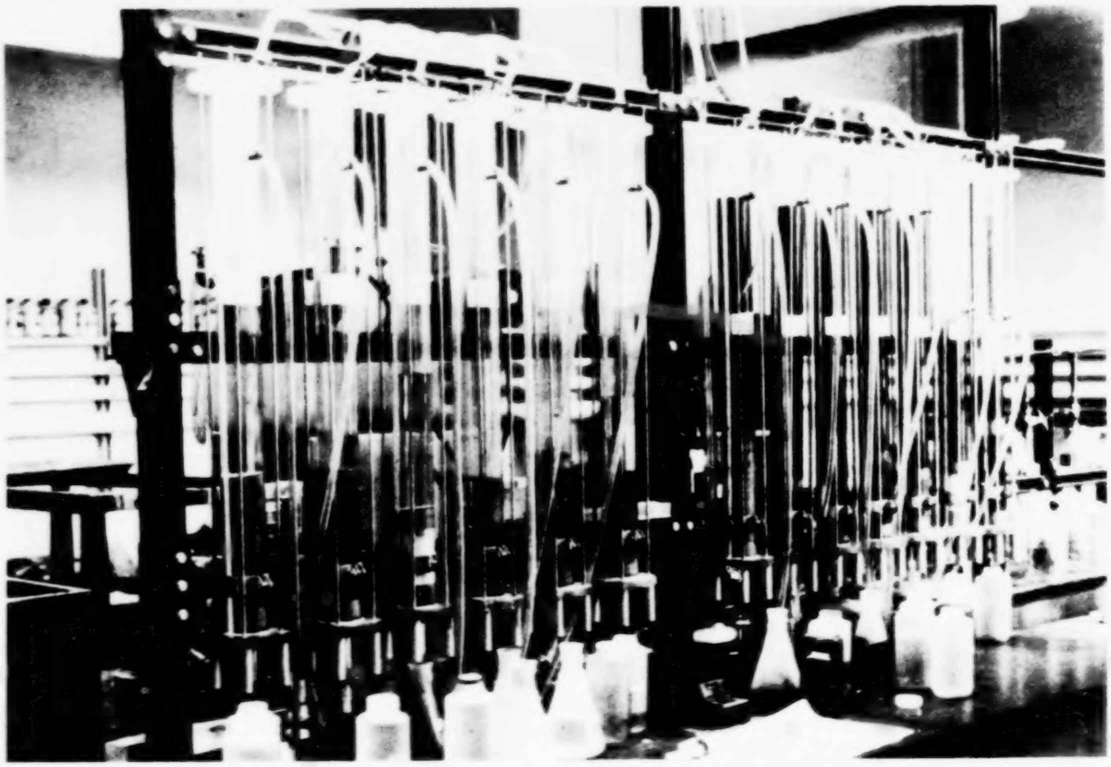

Fig. 1—Laboratory Arrangement of Lysimeters.

0.6 cm thickness) was placed in each column, directly over the drain hole in order to prevent clogging of the outlet and also to support the sorbent material. The column was packed with the preweighted sorbent, placing 3 to 4 cm of Ottawa sand below and above the sorbent to prevent disturbing the geometry of the sorbent column during addition of leachate or water. The packed column was then slowly wetted with leachate to allow total saturation and to force all entrapped air in the soil voids out of the column packing. After a saturation period of at least 24 hours, the column was then filled with leachate to the level of an overflow drain, which had been tapped into the top side of the column, in order to maintain a constant head condition. Leachate was fed to the top of the column through a valved manifold which distributed the leachate to ten lysimeters, simultaneously, from a central reservoir. The central reservoir, a 100 liter polyethylene carboy, delivered the leachate to the manifold system by means of a gravity syphon feed arrangement. Any overflow from the constant head drains was collected and pumped back up to the central reservoir. All tubing in the system was made of Tygon tubing (3/8" i.d.). A constant hydraulic head was maintained in the lysimeters at all times and the volume of leachate passing through the columns was continuously monitored. Samples of leachate effluent were analyzed at predetermined intervals for pH and the concentration of all measurable constituents remaining in the effluent. This was continued until breakthrough for all measurable contaminants had occurred or excessively low permeabilities were encountered. Breakthrough was defined as that condition when the concentration of the species of concern in the collected effluent sample approached or exceeded that in the influent. After breakthrough was achieved, water was continually passed through the sorbent bed until the cations, anions and organics removed by the sorbents were below measurable levels in the effluent. The sorbent capacity exhibited by each sorbent represents the total amount of specific cation, anion or organic retained by the sorbent.

Results and Discussion

Leachate from the calcium fluoride sludge, metal finishing sludge and petroleum sludge, prepared and analyzed (see Table 1) according to procedures described in an earlier report (1) were passed through individual lysimeters that contained one of the following sorbents; acidic fly ash, basic fly ash, zeolite, vermiculite, illite, kaolinite, activated alumina and activated carbon. The volume of effluent from each of these lysimeters were monitored and samples of these effluents were analyzed for pH, calcium, copper, magnesium, zinc, nickel, cadmium, chromium, lead, fluoride, total cyanide and organics. This monitoring and analysis was carried through repeated washings of the sorbents after breakthrough of the leachate had occurred until no measurable contaminants appeared in the wash effluent.

TABLE 1
NATURAL SORBENTS AND THEIR SORBENT CAPACITY FOR REMOVAL OF SPECIFIC CONTAMINANTS IN ACIDIC, NEUTRAL AND BASIC LEACHATES

Ion	*Acidic Leachate (Petroleum Sludge)*		*Neutral Leachate (Calcium Fluoride)*		*Basic Leachate (Metal Finishing Sludge)*	
Ca	Zeolite	(1390)	Zeolite	(5054)	Illite	(1280)
	Illite	(721)	Kaolinite	(857)	Zeolite	(1240)
	Kaolinite	(10.5)	Illite	(0)	Kaolinite	(733)
Cu	Zeolite	(5.2)	Zeolite	(8.2)	Zeolite	(85)
	Acidic F. A.	(2.4)	Kaolinite	(6.7)	Kaolinite	(24)
	Kaolinite	(0)	Acidic F. A.	(2.1)	Acidic F. A.	(13)
Mg	Zeolite	(746)	Basic F. A.	(155)	Zeolite	(1328)
	Illite	(110)	Zeolite	(0)	Illite	(1122)
	Basic F. A.	(1.7)	Illite	(0)	Basic F. A.	(176)
Zn	Zeolite	(10.8)				
	Vermiculite	(4.5)				
	Basic F. A.	(1.7)				
Ni					Zeolite	(13.5)
					Illite	(5.1)
					Acidic F. A.	(3.8)
F	Illite	(9.3)	Illite	(175)	Kaolinite	(2.6)
	Acidic F. A.	(8.7)	Kaolinite	(132)	Illite	(2.2)
	Kaolinite	(3.5)	Acidic F. A.	(102)	Acidic F. A.	(0)
Total CN^-	Illite	(12.1)				
	Vermiculite	(7.6)				
	Acidic F. A.	(2.7)				
COD	Vermiculite	(6654)	Acidic F. A.	(690)	Illite	(1744)
	Illite	(4807)	Illite	(108)	Acidic F. A.	(1080)
	Acidic F. A.	(3818)	Vermiculite	(0)	Vermiculite	(244)

1. Bracket represents sorbent capacity (µg of contaminant removed/g of sorbent used).

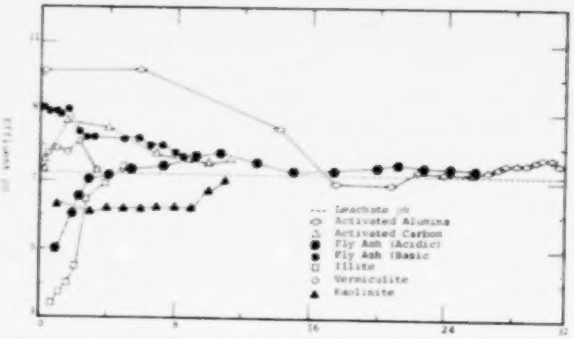

Fig. 2—Lysimeter Studies of pH in Calcium Fluoride Sludge.

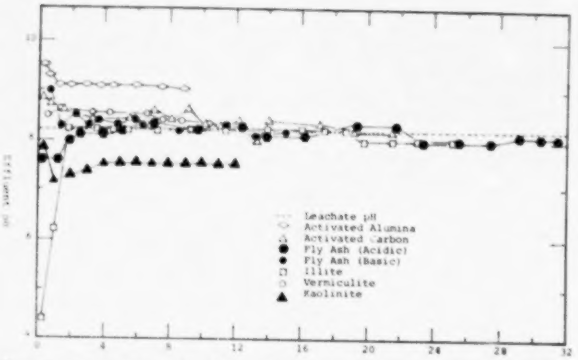

Fig. 3—Lysimeter Studies of pH in Metal Finishing Sludge Leachate.

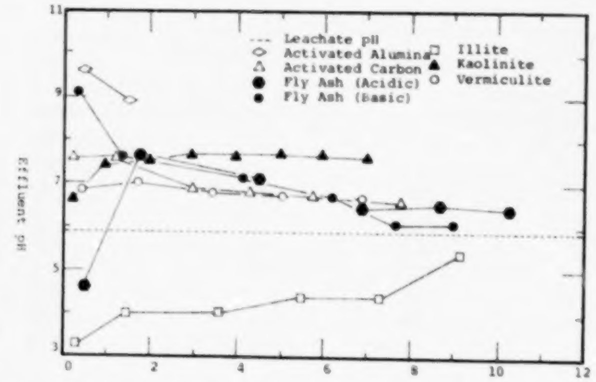

Fig. 4—Lysimeter Studies of pH in Petroleum Sludge Leachate.

The results of monitoring the pH of the effluent using the acidic petroleum sludge leachate, neutral calcium fluoride sludge leachate and basic metal finishing sludge leachate show that in general the sorbents initially define the pH of the leachate. Considerable variations are observed in the pH of the effluents collected initially (see Figures 2, 3 and 4). However, as the leachate is passed through the sorbents in the lysimeters, the pH of the effluent becomes the same as the influent. For example, the effluent from the illite lysimeter is initially acidic, but then attains the pH of the influent leachate (see Figures 2, 3 and 4). Thus, the pH at which the removals of the cations, anions and organics in the industrial sludge leachates occur is regulated initially by the sorbents and finally by the leachate.

The pH of the industrial sludge leachate was found to influence the different sorbent capacities for the removal of the cations, anions and organics present in these leachates. A comparison of the three most promising sorbent capacities for the removal of a specific constituent in each of the three leachates (see brackets in Table 1) shows increases in the removals of calcium, copper and magnesium ions as the pH of the leachate is increased from acidic conditions to alkaline conditions. For example, the zeolite, acidic fly ash and kaolinite sorbent capacities for copper removal are 5.2, 2.4 and 0 respectively in the presence of acidic leachate, but become 8.2, 2.1 and 6.7 μg gm, respectively in the presence of neutral leachate.

The reasons for the zero sorbent capacities exhibited by the illite and zeolite for the calcium and magnesium in the neutral leachate (see Table 1) is not understood at this time.

The influence of pH of the leachate on the different sorbent capacities for the removal of zinc, nickel, iron, cadmium, chromium and lead could not be established in this study. Unfortunately, the measurable concentrations of zinc and nickel were encountered only in the acidic and basic leachates, respectively, whereas the concentrations of iron, cadmium, chromium and lead were all below measurable levels in the three types of leachates examined (see Table 1).

Griffin et al. (2) has also reported similar results. In this study removals of copper, cadmium and zinc increased as the pH of the leachate progressed from acidic to alkaline conditions using only kaolinite and montomorillite. Maximum removals were obtained at about a pH of 8.

The concentration of the contminants in the leachate also influence the sorbent capacity. As the concentration increases, the sorbent capacity also increases. The large zeolite, acidic fly ash and kaolinite sorbent capacities for copper (85, 13 and 24 μg g) obtained in the basic leachate are due both to the influence of pH and the relatively high concentration of copper ion found in this leachate. The copper concentration ranges from 0.43 - 0.53 mg l in this leachate as compared to the acidic and neutral leachates (see Table 2). This influence of concentration on the sorbent capacities is also seen for the other cations and the fluoride anion. The highest concentrations of calcium and fluoride are both encountered in the neutral leachates (see Table 2). The zeolite sorbent capacity for calcium in the neutral leachate is 5054 μg gm as opposed to only 1240 μg gm in the basic leachate even though alkaline conditions favor the removal of cations. Similarly, the illite sorbent capacity for the fluoride is 175 μg gm in the neutral leachate as opposed to 9.3 μg gm and 2.2 μg gm in the acidic and basic leachates respectively.

The influence of the concentration of a specific constituent in the leachate on the sorbent capacities is as expected. If it is assumed that an equilibrium relationship exists between the bound and unbound ions in the

leachate, the higher the ion concentration is in the leachate, the greater the driving force is. As a result, greater amounts of the ion will be removed from the leachate in the presence of a given amount of sorbent.

The sorbent capacities for the removal of the fluoride are also dependent on the pH of the leachate. However, the influence of pH of the leachate on the removal of this anion is opposite to that encountered with cations. Here, sorbent capacities increase as the pH of the leachate decrease from alkaline to acidic conditions. For example, the sorbent capacities for illite, acidic fly ash and kaolinite are 2.2, 2.6 and 0 μg/gm, respectively, for the removal of fluoride in the basic leachate and increases to 9.3, 8.7 and 3.5, respectively in the acidic leachate (see Table 1).

Griffin et al. (2) showed this to be the case for the anion $HAsO_4^{2-}$. Maximum removal of this anion was achieved under acidic conditions around a pH of 6.

The removals of organics also appear to be pH dependent. The sorbent capacities for the removal of COD in both acidic and basic leachates are significantly higher than that achieved with the neutral leachate. However, a trend in the change of sorbent capacity with pH is difficult to identify since the concentration of organics in the acidic leachate is significantly higher than that measured in the basic leachate (see Table 1). Thus, both the pH and concentration of the organics influence the removal of the organics from the acidic leachate.

The pH of the leachate in the lysimeter also influences the leaching of ions from specific sorbents. When the leachate in the lysimeter is initially acidic, as indicated by its effluent pH, the concentration of a specific ion in the effluent was found to exceed the concentration of this ion in the influent. However, as the pH of the effluent approaches the value of 6 and above, the leaching of the specific ion ceases and, in fact, the sorbent actually begins to remove the specific ion that was leached from this sorbent under more acidic conditions. For example, the copper ion was monitored in the effluent from the lysimeters containing acidic fly ash and illite using the acidic, neutral and basic leachates. When the pH of the sorbent approaches 6, as indicated by the pH of its effluent, the illite and acidic fly ash either ceases to leach copper or begins to remove the copper (see Figures 5, 6 and 7). The removal of copper is indicated when its concentration in the effluent falls below the influent concentration. This same behavior is observed for the case of the zinc ion (see Figure 8).

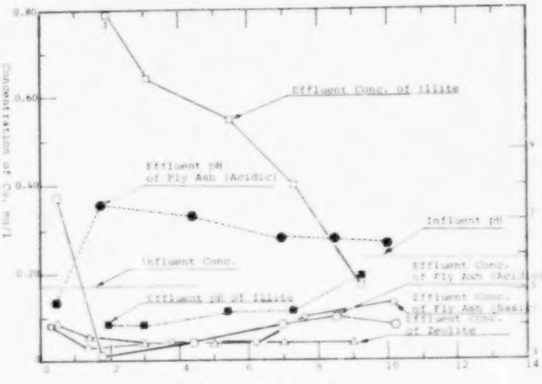

Fig. 5—Effluent Cu Concentration and pH in Lysimeter (Acidic Petroleum Sludge Leachate).

Similar results for fly ash have been recently reported by Theis and Wirth (3). Here, the average release of the heavy metals, zinc, copper, nickel, chromium, lead and cadmium carried out under batch conditions was shown to be minimal at a pH of 6 and above.

Thus, it is obvious from the above results that regulation of the pH of the leachate is essential for optimum removal of the anions, cations and organics while minimizing the leaching of specifications from the sorbents. Initial control of the leachate pH in contact with the sorbents so that it is slightly acidic will favor the removal of anions and organics while minimizing the leaching of specific ions. Further adjustment of the pH of the leachate so that it is slightly alkaline will favor the removal of the cations.

The velocity of the leachate through the sorbent bed in the lysimeters also was found to influence the removal of

TABLE 2

CONCENTRATIONS OF SPECIFIC CATIONS, ANIONS AND ORGANICS ENCOUNTERED IN THE ACIDIC (PETROLEUM SLUDGE), NEUTRAL (CALCIUM FLUORIDE SLUDGE) AND BASIC (METAL FINISHING SLUDGE) LEACHATES

Measured[1] Pollutant	*Acidic Leachate (mg/l)*	*Neutral Leachate (mg/l)*	*Basic Leachate (mg/l)*
Ca	34 - 50	180 - 318	31 - 38
Cu	.09 - .17	.10 - .16	.45 - .53
Mg	27 - 50	4.8 - 21	24 - 26
Ni	below measurable levels		0.15
Zn	.13 - .17	below measurable levels	
F	0.95 - 1.2	6.7 - 11.6	1.2 - 1.5
Total CN	.20 - 1.2	below measurable levels	
COD	251- 340	44 - 49	45 - 50

[1] Fe, Cd, Cr and Pb were analyzed for, but found to be below measurable levels.

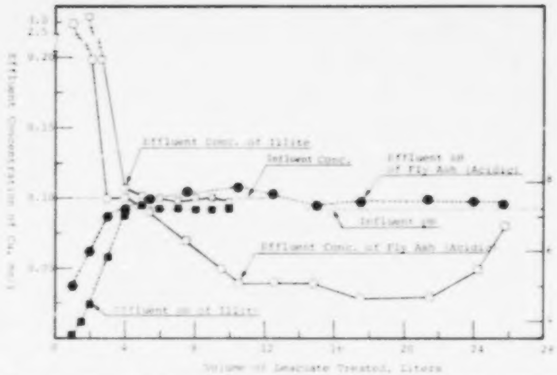

Fig. 6—Effluent Cu Concentration and pH Profile in Lysimeter (Neutral Calcium Fluoride Sludge Leachate).

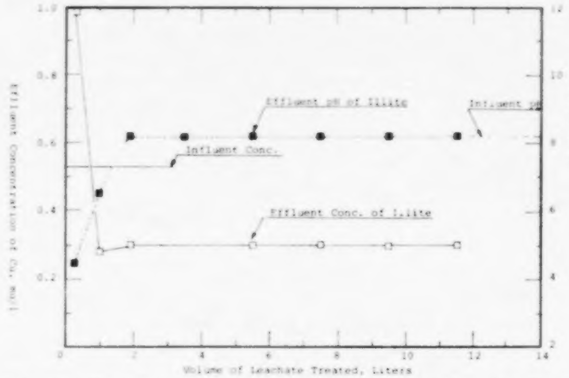

Fig. 7—Effluent Cu Concentration and pH Profile of Illite in Lysimeter (Alkaline Metal Finishing Sludge Leachate).

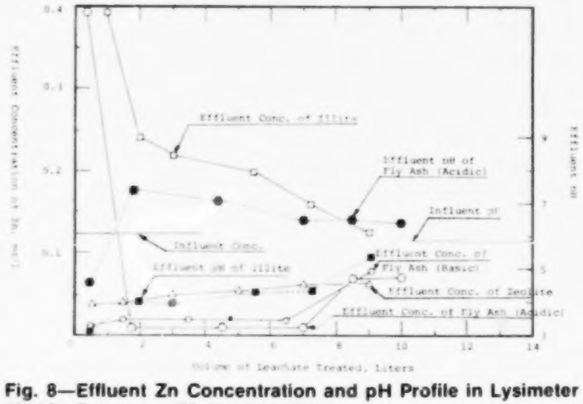

Fig. 8—Effluent Zn Concentration and pH Profile in Lysimeter (Acidic Petroleum Sludge Leachate).

the cations, anions and organics in the leachates. It does not effect the total amount of contaminant that can be removed by a sorbent (sorbent capacity) but it does define the volume of leachate that can be treated with maximum removal of the contaminant. For example, neutral calcium fluoride sludge leachate was passed through four lysimeters that contained different amounts of illite to give different leachate velocities. The fluoride

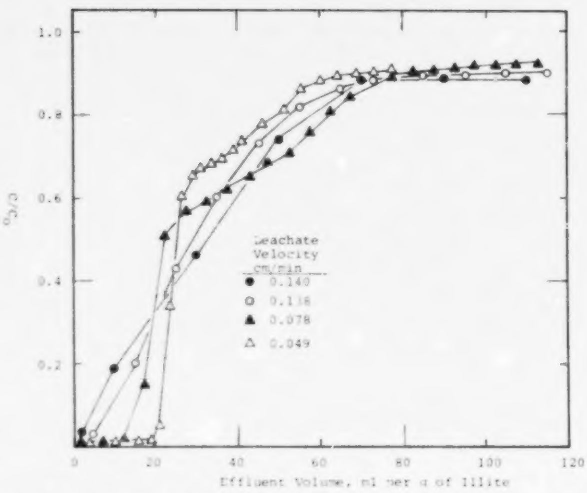

Fig. 9—Effect of Leachate Velocity on the Removal of Fluoride in Calcium Fluoride Sludge Leachate.

concentration in the effluent was monitored until breakthrough was achieved.

The results are shown in Figure 9 where the fraction of fluoride remaining is plotted against the volume of leachate treated per gram of illite used. Here, it is seen that as the leachate velocity decreases, the volume of leachate exhibiting 99 percent fluoride removals, increases. The sorbent capacities however are not influenced by the leachate velocity through the sorbent bed. The different velocities were found to have no significant effect on the sorbent capacity exhibited by the illite for fluoride removals (see Table 3).

An examination of the curves in Figure 8 reveals that the optimum leachate velocity for treating the largest volume of leachate with maximum fluoride removal should be less than 0.042 cm/min. The curve representing operation at the optimum leachate velocity should allow the greatest volume of leachate to be treated with an almost instantaneous decrease in removal efficiency (or rise in C/Co to breakthrough) if one compares the curves obtained for each leachate velocity.

The most effective natural sorbents for the removal of each cation, anion or organics present in measurable quantities in the acidic, neutral and basic leachate is listed in Table 4. There is no single sorbent that can remove all

TABLE 3
Sorbent Capacity Exhibited by Illite For Removal of Fluoride At Different Leachate Velocities Through Sorbents

Leachate Velocity Through the Bed (cm/min)	*Sorbent Capacity* µg/g
.140	190
.138	186
.079	179
.042	175

the measurable constituents present in the three leachates. The combination of zeolite, illite and vermiculite are the most effective for treating the acidic leachate, zeolite, illite, and the acidic and basic fly ashes are the most effective for treating the neutral leachate, and zeolite, illite and kaolinite are the most effective for treating the basic leachate.

The above various combinations which are effective in treating one leachate can also be used to treat the other leachates. However, optimum removal of a specific constituent for a given weight of sorbent would not be achieved because the magnitude of the sorbent capacities are influenced by the pH of the leachate. Thus, a sorbent such as illite which is the most effective for removing the fluoride ion in the acidic and neutral leachate could also be used for removing the fluoride in the basic leachate. However, it would be less effective than kaolinite (see Table 1).

The removal capacities exhibited by the most effective natural sorbents for the removal of the cations, anions and organics are comparable to the more expensive refined sorbents activated alumina and activated carbon in all cases with the exception of the removal of the fluoride ion in the basic leachate (see Table 4). Here, the sorbent capacity exhibited by the activated alumina is some four times that exhibited by the kaolinite.

The above results are significant in that they indicate that the inexpensive natural sorbents can be utilized in the same manner and are as effective as the more expensive activated alumina and activated carbon for the treatment of leachates from industrial sludges. In addition, regeneration of these sorbents is not required; thus the capital investments associated with the regeneration equipment commonly used with activated alumina and activated carbon can be avoided.

Unfortunately, the natural sorbents that are effective for the removal of zinc in the basic leachates and nickel in the acidic and neutral leachates as well as iron, cadmium, chromium and lead could not be defined. These ions were found to be below measurable levels in the leachates obtained from the industrial sludges selected for this investigation.

Although the above results show that natural clay-fly ash combinations are feasible for treating acidic, neutral and basic industrial sludge leachates, only the combination that would provide optimum removals of the cations, anions and organics in calcium fluoride sludge leachate was further investigated. The most effective sorbents (zeolite, acidic and basic fly ashes and illite) were combined in different proportions in a layered

TABLE 4
COMPARISON OF CAPACITIES OF THE MOST EFFECTIVE NATURAL SORBENT WITH ACTIVATED ALUMINA AND ACTIVATED CARBON FOR REMOVAL OF SPECIFIC CONTAMINANTS IN ACIDIC, NEUTRAL AND BASIC LEACHATES

Ion	*Acidic Leachate (Petroleum Sludge)*		*Neutral Leachate (Calcium Fluoride)*		*Basic Leachate (Metal Finishing Sludge)*	
Ca	Zeolite	(1390)[1]	Zeolite	(5054)	Illite	(1280)
	Act. Al.	(200)	Act. Al.	(6140)	Act. Al.	(737)
	Act. Carbon	(128)	Act. Carbon	(357)	Act. Carbon	(212)
Cu	Zeolite	(5.2)	Zeolite	(8.2)	Zeolite	(85)
	Act. Al.	(.35)	Act. Al.	(2.9)	Act. Al.	(6.2)
	Act. Carbon	(0)	Act. Carbon	(2.0)	Act. Carbon	(16.8)
Mg	Zeolite	(746)	Basic F. A.	(155)	Zeolite	(1328)
	Act. Al.	(107)	Act. Al.	(514)	Act. Al.	(495)
	Act. Carbon	(8.6)	Act. Carbon	(3.0)	Act. Carbon	(188)
Zn	Zeolite	(10.8)				
	Act. Al.	(.40)				
	Act. Carbon	(1.1)				
Ni					Zeolite	(13.5)
					Act. Al.	(2.3)
					Act. Carbon	(4.7)
F	Illite	(9.3)	Illite	(175)	Kaolinite	(2.6)
	Act. Al.	(3.4)	Act. Al.	(348)	Act. Al.	(11.4)
	Act. Carbon	(1.2)	Act. Carbon	(0)	Act. Carbon	(0)
Total CN	Illite	(12.1)				
	Act. Al.	(0)				
	Act. Carbon	(2.4)				
COD	Vermiculite	(6654)	Acidic F. A.	(690)	Illite	(1744)
	Act. Al.	(411)	Act. Al.	(0)	Act. Al.	(0)
	Act. Carbon	(1270)	Act. Carbon	(956)	Act. Carbon	(1476)

1. Brackets represent sorbent capacity (μg of contaminant removed/gram of sorbent used).

system to define the optimum arrangement for removal of the measurable cations, anions and organics present in this leachate.

The two sorbent combinations selected were: (1) illite, acidic and basic fly ashes and (2) illite, acidic fly ash and zeolite. These were placed in lysimeters in a layered system in the weight ratios of 1:1:1 or 2:2:1 with the illite being the top layer followed by acidic fly ash and either basic fly ash or zeolite forming the bottom layer. The basic fly ash or zeolite was placed at the bottom to remove the cations such as zinc and copper that are initially leached from the illite and acidic fly ash during the period when the leachate is acidic (see Figure 5, Figure 8). Both the basic fly ash and zeolite show zinc and copper removal during the initial period when these ions are leaching from the illite and acidic fly ash.

The sorbent capacities exhibited by the different clay-fly ash combinations reveal the 2:2:1 ratio of the illite, acidic fly ash and zeolite to be the most effective for removing all the measurable contaminants in the calcium fluoride sludge leachate followed by the 2:2:1 ratio of the illite, acidic and basic fly ashes combinations with the exception of total cyanide (see Table 5).

A different calcium fluoride sludge leachate was used in this portion of the investigation because the volume of leachate required for this study was greater than the volume of leachate that remained from the earlier studies. Analysis of this leachate reveal the presence of measurable concentrations of total cyanide (see Table 6) and zinc which could not be measured in the earlier leachate (see Table 2) even though both sludge leachates were obtained from the same source but at different times. Discussions with the plant personnel revealed that zinc and cyanide were used in several of their processes during the period that this sludge was collected.

Conclusions

The combination of illite, vermiculite and zeolite, the combination of illite, acidic fly ash and zeolite, and the combination of illite, kaolinite and zeolite have been found to be the most effective in a layered system for removing the cations, anions and organics in acidic petroleum sludge leachate, neutral calcium fluoride sludge leachate and basic metal finishing sludge leachate respectively. The combinations of natural clay and fly ash are used because no single sorbents can remove all of the contaminants present in the industrial sludge leachates examined. Any of the above combinations can be used to treat other leachates but they would be as effective as the selected ones because their removals are pH dependent.

Both pH control of the leachate and the order that the natural clays and fly ashes are used in a layered bed affect the removal of the cations, anions and organics in the industrial sludge leachates. Acidic sorbents such as illite, kaolinite and acidic fly ash which can initially induce slightly acidic conditions into the leachate are placed at the top of the layered system followed by those sorbents which can induce slightly alkaline conditions in the leachate. This results in the removal of the anions before the cations. Slightly acidic conditions (greater than pH 6) and slightly alkaline conditions (less than pH 9) favor the removal of anions and cations, respectively. Organics are effectively removed under both acidic and basic conditions.

TABLE 5
Removal Capacities[1] of Combined Sorbents In Lysimeter for Neutral Calcium Fluoride Sludge Leachate

Measured Parameters	*Description*	*I+Fa+Fb* 1:1:1	*I+Fa+Fb* 2:2:1	*I+FA+Z* 2:2:1
Ca	Sorbent Capacity	0	0	406
Mg	Sorbent Capacity	849	515	866
Zn	Sorbent Capacity	5.9	6.1	9.5
F^-	Sorbent Capacity	110	128	148
Cn^-	Sorbent Capacity	1.3	3.9	1.7
COD	Sorbent Capacity	199	241	218

Remarks: (1) Sorbent Capacities are expressed in g of contaminant removal per gram of sorbent used. I = Illite, Fa = Fly Ash (Acidic), Fb = Fly Ash (Basic), Z = Zeolite.
(2) Cd, Cr, Cu, Fe, Ni, and Pb were analyzed and found to be below measurable levels.

TABLE 6
Analysis of the Neutral Calcium Fluoride Sludge Leachate Used for Obtaining Sorbent Combinations to Provide Optimum Treatment

Measured Pollutant[1]	*Concentration (mg/l)*
Ca	119
Mg	89
Zn	0.31
F	15.5
CN	0.61
COD (Organics)	36

1. Cr, Cr, Cu, Fe, Ni and Pb were analyzed for, but found to be below measurable levels.

Alkaline conditions at the base of the bed are desirable. This favors the removal of both the cations in the leachate and the heavy metal cations initially leached from specific sorbents at leachate conditions below pH of 6. Either zeolite or basic fly ash was found effective in controlling this initial leaching of heavy metal ions by the acidic sorbents.

In the design of a sorbent system, the total amount of a specific cation, anions or COD that is removed by a sorbent is indicated by the sorbent capacity. This property is influenced by pH and the concentration of the contaminant in the leachate. The volume of leachate that can be treated with maximum removal is regulated by the velocity of leachate through the sorbent bed. This leachate velocity can be controlled by sorbent bed height, varying the amount of inert material added to the clays to regulate their permeability, or varying the particle size of the sorbents in the bed.

The material costs of the illite-acidic fly ash-zeolite combination, and illite-acidic fly ash-basic fly ash combination, in the weight ratios of 2:2:1, required for the treatment of the leachate from calcium fluoride sludge during a ten-year period of working the landfill have been estimated. They are $2.20 per ton of sludge and $0.62 per ton of sludge, respectively, based upon annual rainfall of 40 inches, assuming that all the rainfall that falls upon the landfill becomes leachate. The illite-acidic fly ash-basic fly ash combination is significantly cheaper than the illite-acidic fly ash-zeolite combination because the fly ash is a waste product.

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The Effectiveness of Fixation Techniques In Preventing the Loss of Contaminants From Electroplating Wastes

Philip G. Malone, Richard B. Mercer & Douglas W. Thompson*

ABSTRACT

A sample of untreated sludge from an electroplating operation and four samples of the same sludge that had been processed in different ways to prevent the loss of toxic metals were tested to evaluate the effectiveness of fixation processes in preventing the escape of metals. Two types of tests were employed, a shake or elutriate test and a long-term (approximately two-year duration) column leaching test. In the elutriate test none of the processes using additives only, effectively immobilized all the toxic metals studied. All samples of fixed sludge showed elevated levels of chromium. The encapsulated sample was not tested in the shake or elutriate test. Column leach testing demonstrated that a plastic encapsulation system offered the best overall containment of toxic metals. Some of the leachate sample from the encapsulated sludge did show slightly elevated cadmium levels; but, in general toxic metal levels in leachate were very low. The fraction of the original chromium and copper lost into the leachate was lowest in the encapsulation system.

INTRODUCTION

Safe disposal of sludges produced from electroplating and metal finishing operations have in the past presented problems with regard to contamination of surrounding soil and groundwater. Cases where metals, especially cadmium and chromium, have escaped into groundwater have been well-documented. Both of these metals are recognized as toxic to humans even in low concentrations (1). The maximum allowable concentration of chromium in drinking water is 0.05 ppm; for cadmium the maximum level is 0.01 ppm.

At Douglas, Michigan, water from wells on the west side of town, near a disposal area used by a metal plating concern, began to turn yellow. Levels of chromate had reached 10.8 ppm when the wells were removed from service by the Michigan Department of Health (2). In another case in Nassau County, New York, plating wastes were releasing both cadmium and chromium to the groundwater (3, 4, 5). Chromium concentrations in groundwater samples reached 49 ppm and cadmium levels reached 10 ppm. Miller, Deluca and Tessier (5) reported that at one location in New Jersey a domestic well near a plating waste lagoon yielded water samples that contained 150 ppm chromium. Less spectacular problems have been caused by copper, fluoride, nitrate, and phenol associated with plating and metal finishing wastes.

The present investigation was undertaken to assess the usefulness of commercially available fixation techniques to prevent the loss of contaminants, especially toxic metals, from plating wastes that are to be landfilled. Parts of this work have been reported in previous publications (6, 7, 8, 9). The waste material treated here is a sludge produced by a plating plant waste water treatment system. The physical and chemical properties of the samples are summarized in Table 1 and bulk analyses for metals are presented in Table 2. The waste includes materials derived from plating, phosphatizing and metal cleaning processes. The major wastes contributed by the plating operations are metal hydroxides produced from the reduction and precipitation of chromate-based plating solutions and wastes from the destruction of cyanide-based plating and rinsing solutions (containing cadmium, copper, and zinc). X-ray diffraction examination showed that the principal crystalline phases present were gypsum ($CaSO_4 \cdot 2H_2O$), quartz, and traces of clay. The metal hydroxides present are not crystallized and do not appear in X-ray diffraction patterns.

Two types of chemical leaching tests were undertaken on the raw and fixed sludges to estimate the release of pollutants to contacting water. In one test procedure, the raw and fixed sludges were shaken with distilled water and the contacting water was filtered and analyzed. In the second procedure the raw and fixed sludges were placed in 150 cm × 10 cm plexiglas leaching columns and water, saturated with CO_2, was permitted to flow around or through the sludge for more than two years. The leachate was collected continuously and aliquots were analyzed at

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progressively lengthening intervals during the test period. The data obtained from these tests were used to evaluate the effectiveness of the fixation procedures in slowing the loss of contaminants into contacting water.

METHODS AND MATERIALS

Preparation of Fixed Material

All of the fixation procedures used in this investigation are proprietory; therefore, details on the exact proportions and exact composition of some of the additives are not available. The general nature of each fixation process has been made available by the processors involved (6). Figure 1 shows the raw and processed sludge samples.

Process A - This process has been patented and uses flyash and a specifically prepared, lime-based additive to produce a pozzolan (concrete-like) material. The sludge remains alkaline during the entire process. The sludge was dewatered by settling and approximately 50 kilograms of fixed material was prepared and cast into 7.6 cm × 40 cm cylinders using standard concrete-testing molds. Process A fixed material was cured under conditions of controlled humidity for 30 days. The finished product contained 25% by weight dry sludge solids.

TABLE 1
SUMMARY OF MAJOR PHYSICAL AND CHEMICAL PROPERTIES OF ELECTROPLATING WASTE

Sludge	*Specific gravity*	*% Solids*	*Coefficient** of permeability (cm/sec)*	*Slurry* pH*
Raw	2.70	23.00	2.2 × 10^{-6}	7.2
Process A	2.49	77.10	4.0 × 10^{-7}	7.5
Process B	2.73	54.47	1.1 × 10^{-5}	7.8
Process C	1.77	69.83	1.1 × 10^{-4}	5.1
Process D	1.18	100.00	--	--

-- = Not available.
* = From the elutriate test (8).
** = Data from (9).

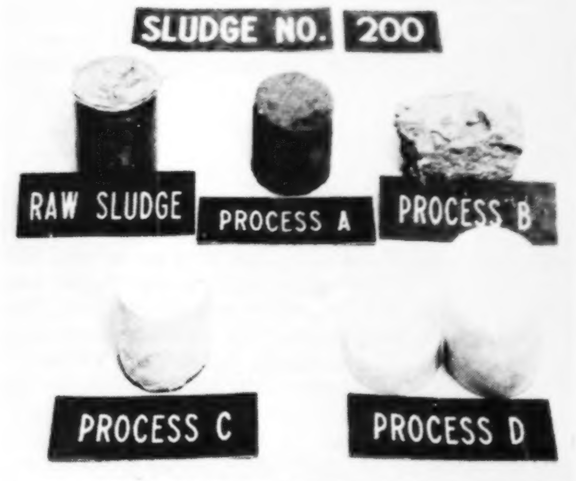

Figure 1. Examples of raw and fixed electroplating wastes.

Process B - This process is patented and uses two alkaline additives, one a liquid and one a solid to produce a soil-like material. The fixed material was cast in a 120 cm × 120 cm × 9 cm block, covered with a polyethylene sheet and allowed to cure for 12 days. The finished product contained 90% dry sludge solids by weight.

Process C - Process C is an organic resin solidification system. Formation of the polymerized resin required that the residue be acidified. The sludge-resin mixture polymerized rapidly and no particular time period was allowed for curing. The finished product contained 67% dry sludge solids by weight.

Process D - This process is an encapsulation method using an organic resin to cement the waste into a solid mass. The solid mass is then inclosed in a 60 mm-thick layer of plastic. Process D requires dry sludge and special molding equipment. Cylinders prepared for laboratory testing were 7.6 cm in diameter and 10 cm in height. Each cylinder contained 250 grams of dried sludge, the dry sludge accounted for 50% by weight of the fixed sludge cylinder.

TABLE 2
BULK ANALYSES OF RAW AND FIXED ELECTROPLATING PLANT SLUDGE

Process	*Wet weight* of material (gm)*	*As (mg/kg)*	*Cd (mg/kg)*	*Cr (mg/kg)*	*Cu (mg/kg)*	*Hg (mg/kg)*	*Mn (mg/kg)*	*Ni (mg/kg)*	*Pb (mg/kg)*	*Zn (mg/kg)*
Raw	12,305	24.0	687	57,830	36,483	0.53	155	2,443	557	6,800
Process A	7,385	29.0	253	18,333	9,600	0.20	122	850	346	2,023
Process B	7,264	13.0	407	46,500	30,183	0.26	383	1,957	480	5,533
Process C	6,409	2.6	102	14,167	6,833	0.04	32	480	170	1,387
Process D	1,252	--	--	--	--	--	--	--	--	--

--= Not available.
* = Refers to weight of material placed in leaching columns for testing.

Note that the fixation process often results in considerable dilution of the waste (Table 2). Fixation may result in an increase, not a decrease, in permeability (Table 1).

Elutriate Test Procedure

A procedure for a rapid, distilled water shaking or elutriate test was developed to provide a preliminary assessment of the effectiveness of fixation. Two hundred milliliter subsamples of raw sludge were mixed with 800 ml at 2500 rpm for 20 minutes and the centrifugate was filtered through a 0.45-micron membrane filter. The fixed sludges, with the exception of samples from process D, were broken into random-sized pieces and 200 grams of fixed material was shaken with distilled water using a procedure identical to that used with the raw sludge. No attempt was made to run an elutriate test on process D samples because of their thick encapsulation. All elutriate tests were conducted in triplicate. The filtrate (or elutriate) from each was preserved by adding nitric acid to lower the pH to 2.0. The analytical procedures used and quality control program for analyses are discussed in detail in a previously published report (6).

Leaching Procedure

Each raw or fixed sludge was divided into subsamples. Three large subsamples of approximately 12 kilograms each were placed in the columns for leach testing. Smaller subsamples were taken for bulk chemical analyses and moisture determinations.

Three identical leaching columns were prepared for the raw sludge and each of the fixed sludges. Data on leachate from only one set of columns are reported here. This set was selected for analysis with techniques allowing very low detection limits. Leachate samples from the other two sets of column were analyzed using conventional flame AA methods and the data were used to confirm the analyses from the set used for low level measurements. The columns were made from 1.5 meter lengths of 10.16 cm ID plexiglas tubing (Figure 2). The bottom of each column was closed with a perforated plate that allowed the leachate to drain into a 1.27 cm deep collecting well. The leaching fluid was introduced through a tube entering the leach column 19 cm from the top of the column. The tops of the columns were covered with loose-fitting plastic lids to prevent dust from entering. The flow of leachate water through each column was regulated with a teflon stopcock. The bottom 7.5 cm of each column was packed with 60 mm diameter polypropylene pellets to retard the movement of particulate material into the collecting well. Leachate from each column was collected in a 4.5 liter polyethylene bottle located below the column.

The raw sludge was placed in the columns directly and back-flooded with distilled water to remove all air bubbles. The fixed sludge samples that were not cast into cylinders (i.e., the samples from Processor B) were broken into conveniently-handled pieces and placed in the columns. The fixed sludges that had been cast into

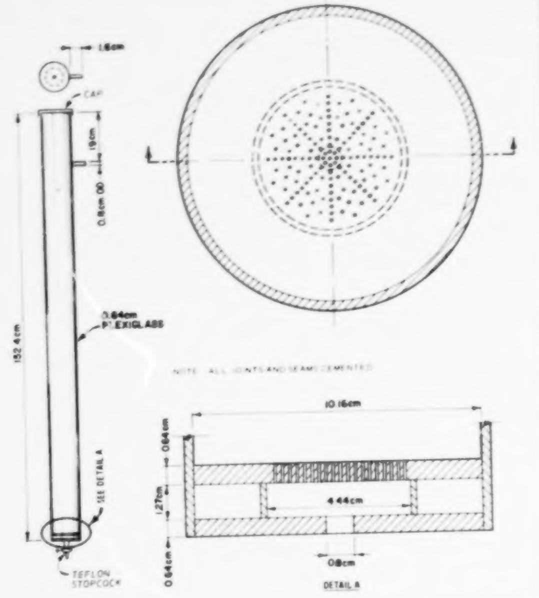

Figure 2. Design of leaching column.

TABLE 3
TECHNIQUES USED IN ANALYSES

Chemical species	*Procedures and/or instrumentation**	*Limits of detection (ppm)*
As	Determined with a Nisseisangyo Zeeman Shift Atomic Absorption Spectrophotometer	0.005
Cd	Determined with a Perkin-Elmer Heated Graphite Atomizer Atomic Absorption Unit	0.0003
Cr	Same as above	0.005
Cu	Same as above	0.003
Hg	Determined with a Nisseisangyo Zeeman Shift Atomic Absorption Spectrophotometer	0.0002
Mn	Determined with a Perkin-Elmer Heated Graphite Atomizer Atomic Absorption Unit	0.03
Ni	Same as above	0.05
Pb	Same as above	0.002
Zn	Same as above	0.05

*Mention of trade names or commercial products does not constitute endorsement or recommendation of use.

TABLE 4
AVERAGE CONCENTRATIONS OF METALS IN ELUTRIATE SAMPLES FOR RAW AND FIXED ELECTROPLATING SLUDGE

Fixation process	*pH*	*As* (ppm)*	*Cd (ppm)*	*Cr (ppm)*	*Cu (ppm)*	*Hg (ppm)*	*Mn (ppm)*	*Ni (ppm)*	*Pb (ppm)*	*Zn (ppm)*
Raw sludge	7.2	<0.005	0.39	0.69	16.00	<0.0002	4.10	4.10	0.020	7.80
Process A	7.5	0.080	0.38	3.90	4.70	0.0002	0.99	0.56	0.250	6.20
Process B	7.8	0.008	0.59	59.00	13.00	<0.0002	1.50	0.84	0.740	5.00
Process C	5.2	0.060	25.00	21.00	1200.00	<0.0002	11.00	120.00	<0.002	330.00

* Each reported analyses is the average of three samples.

cylinders (i.e., material from Processors A, C and D) were placed in the columns and polypropylene pellets were packed around the cylinders. The variations in column loading procedures were made to accommodate those processors (A, C, and D), who required their samples be tested as a monolithic mass rather than as fragmented or ground material. In each case the processor felt that the material, as packed in the columns, reflected the way the material would be placed in a landfill.

The leaching liquid used in this test was deionized, distilled water saturated with carbon dioxide. The pH of this solution is approximately 4.5. Where possible, flow through the columns was maintained in a range approximating the rate of flow through the covering material on a landfill; 7 to 70 ml per day for these columns. This is equivalent to an hydraulic conductivity of 1×10^{-5} to 1×10^{-6} cm/sec. In some cases the natural flow rate was less than this amount and in other cases, the flow rate varied unpredictably. If the natural flow rate was lower then desired, the natural rate was allowed to regulate the flow. If the flow was too rapid the stopcock was used to control the flow. If the flow rate was variable, leachate was collected until 4.5 liters had passed through the column; then, the flow of leachate was shut off.

Samples of leachate from the columns were preserved by adding nitric acid to lower the pH to 2.0. The techniques used in analyses are given in Table 3. A detailed discussion of analytical procedures is presented in a previously published report (6).

Procedure for Bulk Digests

Samples of raw and fixed sludges were digested in acid to provide a bulk analysis of the material that was tested. Two grams (wet weight) of material were weighed out and transferred to a covered 100-ml teflon beaker. Fifteen ml of reagent-grade hydrofluoric acid and 10 ml of reagent-grade concentrated nitric acid were added to the sample. The material was heated to 175° C and maintained at this temperature for 2 to 3 hours. After digestion the beaker lids were removed and the samples were evaporated to near dryness and the residue was redissolved in 6N hydrochloric acid. The samples were transferred quantitatively to a 100-ml volumetric flask and brought up to volume with distilled-deionized water. The techniques used for chemical analysis are given in Table 3. Separate subsamples of fresh material were weighed out and percent solids determinations were made to correct the analyses to a mg/kg dry weight basis.

RESULTS AND DISCUSSION

Elutriate Test Results

The results of the elutriate tests performed on the raw and fixed (A, B, and C) electroplating sludges are given in Table 4. Each of the tabulated analyses is the average of three separate elutriate tests. All of the elutriate from the raw and fixed sludges contained more cadmium, chromium, copper, and manganese than would be permitted in a public water supply (Table 5), and in some cases the elutriate samples also exceeded the recommended levels for arsenic, lead and zinc. No standards have been written for nickel in public water supplies, but the levels observed in the elutriates are generally higher than would be considered safe (1).

In some cases, the metal concentrations in the elutriates from the fixed sludges were actually higher than concentrations observed in elutriate samples obtained from the raw sludge. This is especially true for

TABLE 5
PERMISSIBLE LIMITS OF SELECTED METALS IN PUBLIC WATER SUPPLIES*

Metal	*Permissible limit (ppm)*
Arsenic	0.05
Cadmium	0.01
Chromium	0.05
Copper	1.0
Mercury	0.002
Manganese	0.05
Nickel	0.50 **
Lead	0.05
Zinc	5.0

* From (1).

**This level causes damage to plants but no standard has been set for water supplies.

process C, the organic polymer system that required acidification of the sludge. In process C, for all metals reported here, with the exception of lead, the elutriate from the fixed sludge showed higher concentrations than did the elutriate from raw sludge. Process B did not reduce the loss of arsenic, cadmium, chromium or lead; although it did reduce the loss of copper, manganese, nickel and zinc. Process A did not reduce the leaching of arsenic, chromium or lead but did reduce the loss of cadmium, copper, manganese, nickel and zinc. Process D, the plastic encapsulation system, was not evaluated in the elutriate test, so this system cannot be compared in the present study. It can be assumed that if the plastic jacket on the samples remained intact, only the plastic would come into contact with water and no appreciable increase in metals in the elutriate would be observed (other than metals leached from the plastic).

In the three fixation systems examined in the elutriate or shake test, no fixation process succeeded in reducing the concentration of chromium in contacting water below the level observed with raw sludge. Chromium is the major potential hazard in electroplating sludge. Control of the leaching of this metal is critical to treating electroplating wastes.

Column Leaching Test Results

The column leaching test was designed to simulate the effects of leaching raw or fixed sludge in an unlined landfill. Two aspects of potential pollution were examined: a) the concentration of metals to be

TABLE 6
LEACHATE FROM ELECTROPLATING PLANT SLUDGE

COLUMN 005 *RAW*

Sequence	*Day*	*pH*	*Specific Conductance (µ MOHS/cm × 10³)*	*As (ppm)*	*Cd (ppm)*
1	1	--		--	0.0400
2	8	8.3	18.80	<0.005	0.1000
3	14	8.4	--	--	0.1300
4	21	8.2	18.00	<0.005	0.0894
6	39	8.4	2.20	<0.005	0.0696
7	63	8.2	--	--	--
8	91	8.2	18.20	--	--
9	126	8.4	18.00	<0.005	<0.0003
10	189	--	--	--	--
11	245	8.2	15.00	<0.005	--
12	353	8.0	21.00	<0.005	0.0105
13	451	8.5	24.00	<0.005	0.0997
14	569	--	--	--	--
15	708	8.2	21.00	0.077	0.0097
16	814	7.2	23.00	--	--

Sequence	*Cr (ppm)*	*Cu(ppm)*	*Hg (ppm)*	*Mn (ppm)*	*Ni (ppm)*	*Pb (ppm)*	*Zn (ppm)*
1	0.026	2.500	--	0.79	0.30	--	0.28
2	0.015	0.760	--	0.56	2.50	0.077	<0.05
3	0.020	3.211	<0.0002	0.19	0.30	0.052	0.57
4	0.021	3.300	0.0010	0.20	0.40	0.592	0.40
5	--	--	--	--	--	--	--
6	0.019	3.700	0.0022	0.20	<0.05	0.975	<0.15
7	--	--	--	--	--	--	--
8	--	--	--	--	--	--	--
9	<0.005	<0.003	<0.0002	<0.03	0.90	<0.002	--
10	--	--	--	--	--	--	--
11	--	--	--	0.15	--	--	<0.05
12	0.095	1.086	0.0003	0.24	0.15	--	0.14
13	0.078	2.067	<0.0002	0.16	0.07	--	0.10
14	--	--	--	--	--	--	--
15	0.027	0.650	0.0137	0.06	0.05	<0.002	<0.05
16	--	--	--	--	--	--	--

-- = No analysis.

expected in water percolating through landfilled sludge, and b) the fraction of each toxic metal present in the electroplating sludge that might be released from the sludge during approximately two years of leaching. The elutriate test addressed itself only to the problem of the maximum concentration to be expected on the initial contact of sludge with percolating water; the column leach test furnishes confirming data and allows long-term effects to be evaluated. Metal analyses for all leachate samples are presented in Tables 6 - 10. Variations in the concentration of the most important potential pollutant, chromium, are shown graphically in Figures 3 - 7.

Ideally the metal levels in column leachates should always be below levels specified for public water supplies and the leachate samples from fixed sludges should show fewer instances of high metal concentrations than leachate samples from raw sludge. The percentage of leachate samples that exceeded public water supply standards for each of the major toxic metals is given in Table 11. In some cases, the raw sludge column yielded fewer unacceptable leachate samples than did the columns of fixed material. The best results were obtained from the sample fixed by total plastic encapsulation. The worst results were obtained with the fixing process that required acidification of the waste.

In order to judge the efficiency with which selected pollutants were contained in the different sludge samples, the cumulative percent of metal lost was calculated from the concentration of metal in the leachate and the volume of leachate obtained during each sampling interval (Table 12). Table 13 shows the amount of metal lost from the test columns over the total leaching period. Table 14

TABLE 7
LEACHATE FROM ELECTROPLATING PLANT SLUDGE

COLUMN 139 *PROCESS A*

Sequence	*Day*	*pH*	*Specific Conductance (μ MOHS/cm × 10³)*	*As (ppm)*	*Cd (ppm)*
1	14	9.3	14.00	0.007	0.0052
2	21	9.4	0.90	<0.005	0.1045
3	28	8.1	6.00	<0.005	0.0195
4	35	9.0	4.60	<0.005	0.090
5	56	7.4	3.50	<0.005	0.0020
6	77	7.5	3.10	<0.005	<0.0003
7	133	8.3	3.08	<0.005	0.0004
8	161	8.6	2.00	<0.005	<0.0003
9	196	8.1	2.95	0.006	<0.0003
10	259	7.8	2.30	0.006	<0.0003
11	329	7.1	2.00	<0.005	0.0012
12	392	8.3	1.90	<0.005	0.0003
13	476	8.1	2.10	<0.005	0.0004
14	630	7.9	1.93	0.005	--
15	784	7.5	2.10	--	--

Sequence	*Cr (ppm)*	*Cu (ppm)*	*Hg (ppm)*	*Mn (ppm)*	*Ni (ppm)*	*Pb (ppm)*	*Zn (ppm)*
1	1.300	3.600	<0.0002	<0.03	<0.05	0.029	<0.05
2	1.600	1.900	<0.0002	0.90	0.08	0.034	--
3	0.800	1.800	0.0006	<0.03	<0.05	0.004	<0.05
4	0.300	0.956	<0.0002	<0.03	<0.05	<0.002	<0.05
5	<0.005	1.070	0.0006	<0.03	<0.05	<0.002	<0.05
6	0.080	0.880	<0.0002	<0.03	<0.05	0.006	<0.05
7	0.041	0.451	<0.0002	<0.03	<0.05	<0.002	<0.05
8	0.060	0.428	<0.0002	<0.03	<0.05	0.035	<0.05
9	0.057	0.202	<0.0002	<0.03	<0.05	<0.002	<0.05
10	0.226	0.210	<0.0002	<0.03	<0.05	--	<0.05
11	0.241	0.100	0.0003	<0.03	<0.05	<0.002	<0.05
12	0.064	0.182	<0.0002	<0.03	<0.05	<0.002	<0.05
13	0.015	0.209	<0.0002	<0.03	<0.05	<0.002	<0.05
14	0.044	1.100	--	<0.03	<0.05	--	--
15	--	--	--	--	--	--	--

-- = No analysis.

TABLE 8
LEACHATE FROM ELECTROPLATING PLANT SLUDGE

COLUMN 086 *PROCESS B*

Sequence	*Day*	*pH*	*Specific Conductance (μ MOHS/cm × 10^3)*	*As (ppm)*	*Cd (ppm)*
1	7	11.9	20.00	<0.005	0.0050
2	14	11.6	8.80	<0.005	<0.0003
3	21	11.0	6.40	<0.005	<0.0003
4	28	11.2	4.88	<0.005	0.0008
5	42	11.0	4.20	<0.005	--
6	56	12.0	3.00	<0.005	--
7	91	7.5	2.90	<0.005	0.0028
8	126	10.0	2.50	<0.005	<0.0003
9	161	8.6	2.20	<0.005	<0.0003
10	224	9.6	2.20	<0.005	--
11	273	6.9	2.30	<0.005	0.0003
12	365	10.0	2.30	0.011	<0.0003
13	498	7.6	2.30	<0.005	0.0103
14	611	9.5	2.00	<0.005	0.0011
15	735	7.7	1.80	<0.005	0.0170
16	889	8.3	2.00	--	--

Sequence	*Cr (ppm)*	*Cu (ppm)*	*Hg (ppm)*	*Mn (ppm)*	*Ni (ppm)*	*Pb (ppm)*	*Zn (ppm)*
1	23.600	13.600	0.0009	<0.03	0.17	0.381	0.07
2	12.300	4.000	0.0003	<0.03	0.16	--	<0.05
3	6.400	2.400	<0.0002	<0.03	<0.05	0.003	<0.05
4	4.500	2.000	0.0030	<0.03	<0.05	<0.002	--
5	<0.005	2.100	0.0028	<0.03	<0.05	--	<0.05
6	2.850	1.500	<0.0002	<0.03	<0.05	<0.002	<0.05
7	2.000	1.288	0.0002	<0.03	<0.05	<0.002	<0.05
8	3.150	2.740	<0.0002	<0.03	<0.05	--	<0.05
9	0.970	2.560	<0.0002	<0.03	<0.05	<0.002	<0.05
10	1.060	1.820	<0.0002	<0.03	0.56	--	<0.05
11	1.260	1.950	<0.0002	<0.03	<0.05	<0.002	<0.05
12	0.916	2.432	<0.0002	<0.03	<0.05	<0.002	<0.05
13	1.060	2.280	<0.0002	<0.03	<0.05	<0.002	<0.05
14	1.680	1.250	<0.0002	<0.03	<0.05	0.003	<0.05
15	1.710	1.460	--	<0.03	<0.05	--	0.18
16	--	--	--	--	--	--	--

-- = No analysis.

TABLE 9
LEACHATE FROM ELECTROPLATING PLANT SLUDGE

COLUMN 122 *PROCESS C*

Sequence	*Day*	*pH*	*Specific Conductance (μ MOHS/cm × 10^3)*	*As (ppm)*	*Cd (ppm)*
1	7	4.2	15.50	<0.005	21.0000
2	14	4.3	11.10	<0.005	14.9970
3	21	4.4	9.40	<0.005	15.9995
4	28	4.5	4.55	<0.005	8.5000
5	42	5.0	5.70	<0.005	9.0000
6	56	4.5	3.50	<0.005	3.1002
7	91	4.8	4.00	0.010	5.9985
8	126	5.0	3.30	<0.005	5.2994
9	147	5.4	2.50	<0.005	4.3990
10	210	5.0	2.25	<0.005	3.3990
11	266	4.6	2.70	0.026	2.4000
12	364	--	--	0.010	3.1995
13	441	4.9	0.90	<0.005	0.4015
14	518	3.9	1.20	<0.005	0.5240
15	672	4.5	1.80	<0.005	1.1200
16	826	4.5	2.30	--	--

Sequence	*Cr (ppm)*	*Cu (ppm)*	*Hg (ppm)*	*Mn (ppm)*	*Ni (ppm)*	*Pb (ppm)*	*Zn (ppm)*
1	298.800	700.000	0.0030	6.30	123.00	0.697	368.00
2	130.000	800.000	0.0040	2.80	69.50	0.240	200.00
3	78.000	670.000	<0.0002	4.05	69.00	0.138	180.00
4	16.000	30.000	<0.0002	2.40	38.00	<0.002	104.00
5	20.000	310.000	--	1.50	38.00	--	--
6	6.000	180.000	<0.0002	0.90	11.00	0.020	39.00
7	7.000	239.988	<0.0002	1.60	22.00	0.031	73.00
8	3.900	114.940	<0.0002	0.58	12.10	0.037	50.75
9	2.100	159.992	<0.0002	0.76	12.20	0.028	38.50
10	1.990	180.000	<0.0002	0.80	8.82	--	39.30
11	1.890	150.000	<0.0002	0.80	8.27	0.024	27.60
12	2.120	149.992	<0.0002	0.77	7.98	0.066	25.00
13	0.346	35.192	<0.0002	0.99	1.07	--	4.44
14	0.715	42.200	<0.0002	0.10	1.36	0.019	5.00
15	1.460	90.100	--	0.23	2.94	--	11.50
16	--	--	--	--	--	--	--

-- = No analysis.

TABLE 10
LEACHATE FROM ELECTROPLATING PLANT SLUDGE

COLUMN 102 *PROCESS D*

Sequence	*Day*	*pH*	*Specific Conductance (μ MOHS/cm $\times 10^1$)*	*As (ppm)*	*Cd (ppm)*
1	7	7.2	2.40	<0.005	0.0200
2	14	7.1	16.00	<0.005	0.0145
3	21	7.3	4.00	<0.005	0.0027
4	28	7.0	5.10	<0.005	2.4000
5	42	7.4	6.30	<0.005	0.0036
6	56	7.2	4.20	0.008	0.0036
7	91	7.1	1.60	<0.005	0.0017
8	112	7.4	3.30	<0.005	0.0036
9	147	7.2	2.50	<0.005	0.0003
10	210	7.1	3.32	<0.005	0.0007
11	273	7.1	4.20	<0.005	0.0020
12	364	6.4	7.60	0.010	0.0019
13	515	6.9	4.00	0.008	0.0150
14	641	8.0	6.80	0.005	0.0075
15	760	7.7	21.00	0.008	0.0100

Sequence	*Cr (ppm)*	*Cu (ppm)*	*Hg (ppm)*	*Mn (ppm)*	*Ni (ppm)*	*Pb (ppm)*	*Zn (ppm)*
1	--	0.035	--	<0.03	<0.05	--	--
2	<0.005	0.030	<0.0002	<0.03	<0.05	0.003	<0.05
3	<0.005	0.037	<0.0002	<0.03	<0.05	<0.002	--
4	<0.005	<0.003	<0.0002	<0.03	<0.05	<0.002	--
5	<0.005	<0.003	<0.0002	<0.03	<0.05	<0.002	--
6	--	<0.003	<0.0002	<0.03	<0.05	<0.002	<0.05
7	<0.005	<0.003	<0.0004	<0.03	<0.05	<0.002	<0.05
8	<0.005	<0.003	<0.0002	<0.03	<0.05	<0.002	<0.05
9	<0.005	<0.003	<0.0002	<0.03	<0.05	--	<0.05
10	<0.005	0.007	<0.0002	<0.03	<0.05	0.397	<0.05
11	<0.005	0.038	<0.0002	<0.03	<0.05	--	<0.05
12	<0.005	0.020	<0.0002	<0.03	<0.05	--	<0.05
13	<0.005	0.023	<0.0002	<0.03	<0.05	0.004	<0.05
14	<0.005	0.012	<0.0002	<0.03	<0.05	0.002	<0.05
15	<0.005	0.007	<0.0002	<0.03	<0.05	<0.002	<0.05

--= No analysis.

shows the amount of each constituent lost as a cumulative fraction of the amount initially available. In many cases, the fraction of metal lost through leaching was larger in the processed sludges than in the raw sludge. Only process D, the encapsulation system, prevented the escape of copper or chromium. None of the fixing systems could prevent a relatively large release of cadmium. The leachate from the encapsulated samples (Process D) showed surprisingly high levels of cadmium. The encapsulation process is so effective in preventing the escape of chromium and copper that it seems unlikely that the cadmium found in the leachate is escaping from the encapsulated sludge. Possibly, cadmium is present in a catalyst or plasticizer used to form the plastic jacket or may be used in the molds or release compounds used in the manufacture of the cylinders.

TABLE 11
PERCENTAGE OF LEACHATE SAMPLES EXCEEDING CONCENTRATIONS RECOMMENDED FOR PUBLIC WATER SUPPLIES

Constituent	*Raw sludge*	*Process A*	*Process B*	*Process C*	*Process D*
As	12	0	0	7	0
Cd	78	23	17	100	27
Cr	22	71	93	100	0
Cu	67	36	100	100	0
Hg	28	0	14	15	0
Mn	90	7	0	100	0
Pb	67	0	10	36	9
Zn	0	0	0	86	0

TABLE 13
TOTAL AMOUNT OF SELECTED METALS LEACHED FROM RAW AND FIXED SLUDGE

Metal	*Raw sludge (mg)*	*Process A (mg)*	*Process B (mg)*	*Process C (mg)*	*Process D (mg)*
Cd	0.14	0.41	0.56	221.59	4.28
Cr	0.23	10.25	231.25	1938.52	0.01
Cu	6.06	29.83	152.71	8623.86	0.60

TABLE 14
CUMULATIVE FRACTION OF SELECTED METALS LEACHED FROM RAW AND FIXED SLUDGE

Metal	*Raw sludge*	*Process A*	*Process B*	*Process C*	*Process D*
Cd	$7.20 \times 10^{[illegible]}$	$2.83 \times 10^{[illegible]}$	$3.49 \times 10^{[illegible]}$	$4.85 \times 10^{[illegible]}$	$5.49 \times 10^{[illegible]}$
Cr	$1.42 \times 10^{[illegible]}$	$9.82 \times 10^{[illegible]}$	$1.26 \times 10^{[illegible]}$	$3.06 \times 10^{[illegible]}$	$1.59 \times 10^{[illegible]}$
Cu	$5.87 \times 10^{[illegible]}$	$5.45 \times 10^{[illegible]}$	$1.28 \times 10^{[illegible]}$	$2.82 \times 10^{[illegible]}$	$1.32 \times 10^{[illegible]}$

The column leaching indicates that the encapsulation process is the most dependable system for preventing unacceptable metal levels from occurring in leachate and for preventing large long-term leaching losses. This test agrees with similar leaching experiments reported in the literature (10). Both the elutriate test and the column leaching tests indicate systems involving additives without encapsulation are far less effective and in some cases the processed material may leach metals more rapidly than raw sludge.

TABLE 12
VOLUMES OF LEACHATE COLLECTED FROM ELECTROPLATING PLANT SLUDGE COLUMNS

Process Column	*Raw 005*		*Process A 139*		*Process B 086*		*Process C 122*		*Process D 102*	
Sequence	*Time (Days)*	*Volume (Liters)*	*Time (Days)*	*Volume (Liters)*	*Time (Days)*	*Volume (Liters)*	*Time (Days)*	*Volume (Liters)*	*Time (Days)*	*Volume (Liters)*
1	1	0.14	14	1.69	7	4.50	7	2.17	7	2.15
2	8	0.26	21	1.98	14	4.50	14	2.17	14	2.08
3	14	0.29	28	1.69	21	2.24	21	1.96	21	1.86
4	21	0.22	35	1.86	28	2.05	28	3.18	28	1.86
5	28	0.21	56	1.98	42	2.24	42	2.15	42	1.55
6	29	0.22	77	2.05	56	2.46	56	3.06	56	1.86
7	63	0.16	133	2.55	91	1.69	91	1.60	91	2.29
8	91	0.64	161	4.50	126	2.38	126	1.94	112	1.62
9	126	0.24	196	0.83	161	1.77	147	1.76	147	1.53
10	189	–	259	4.50	224	2.03	210	3.49	210	3.32
11	245	2.98	329	3.41	273	3.10	266	3.15	273	2.27
12	353	1.69	392	4.50	365	4.50	364	–	364	4.50
13	451	–	476	4.50	498	4.50	441	4.50	515	4.50
14	569	–	630	4.50	611	3.92	518	4.50	641	4.50
15	708	1.86	784	4.50	735	4.50	672	4.50	760	4.50
16	814	–	–	–	889	4.50	826	4.50	–	–

– = Not reported.

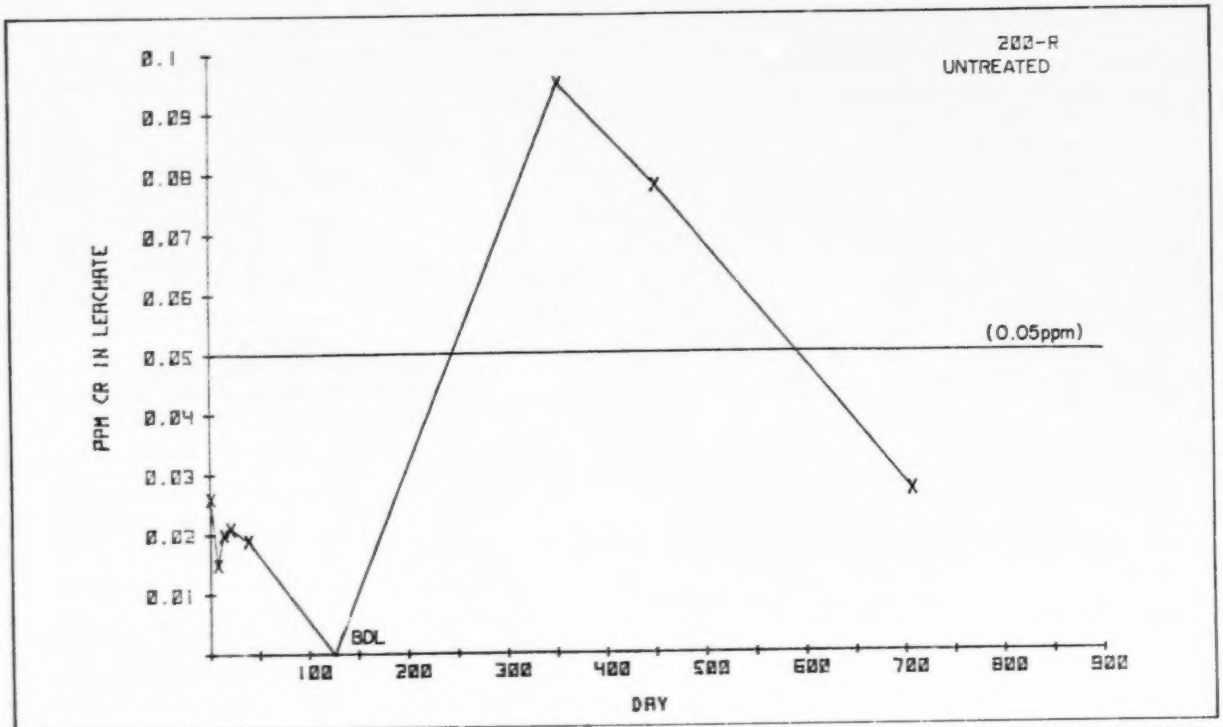

Figure 3. Variation in concentration of chromium in leachate from untreated (raw) sludge with time. Horizontal line at 0.05 ppm indicates public water supply standard.

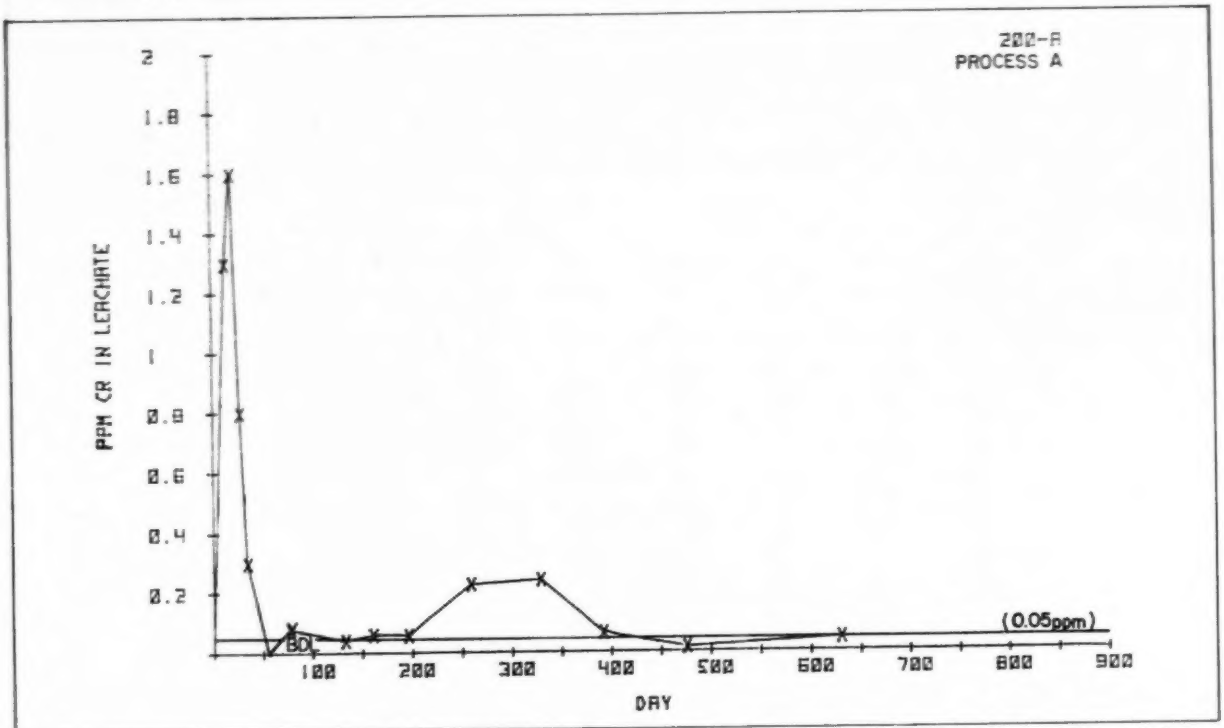

Figure 4. Variation in concentration of chromium in leachate from process A fixed sludge with time. Horizontal line at 0.05 ppm indicates water supply standard.

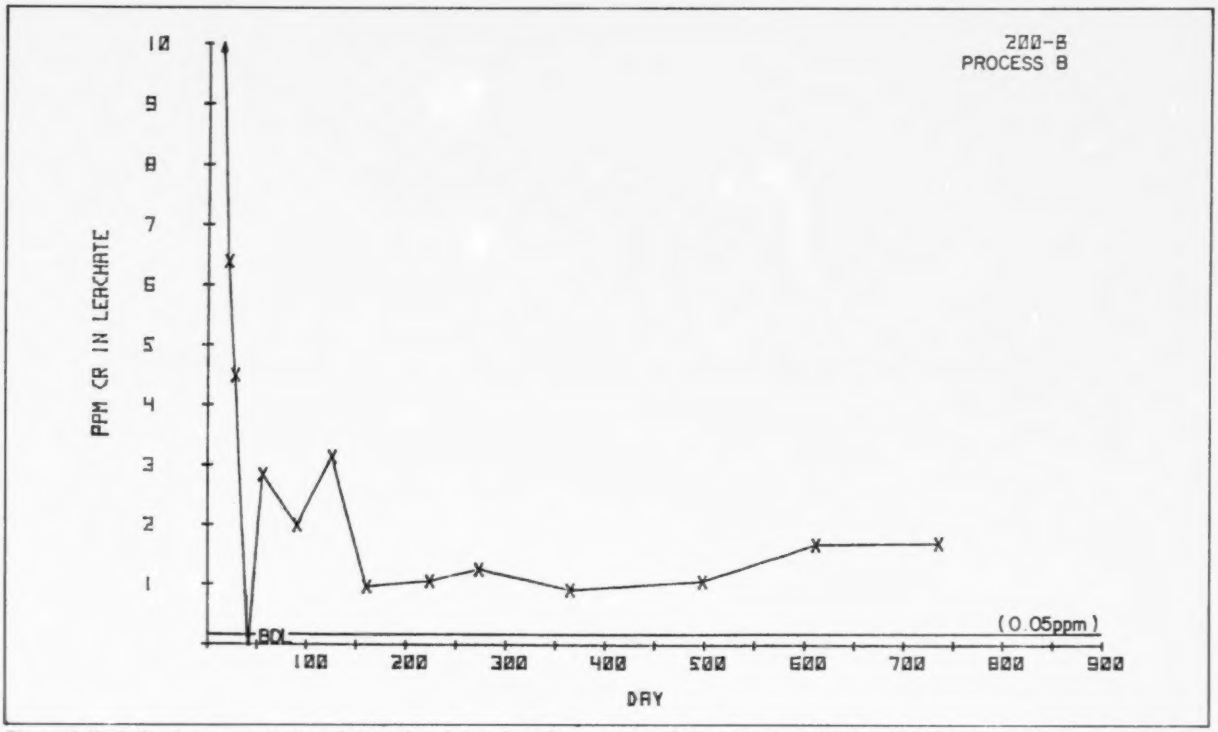

Figure 5. Variation in concentration of chromium in leachate from process B fixed sludge with time. Horizontal line at 0.05 ppm indicates public water supply standard.

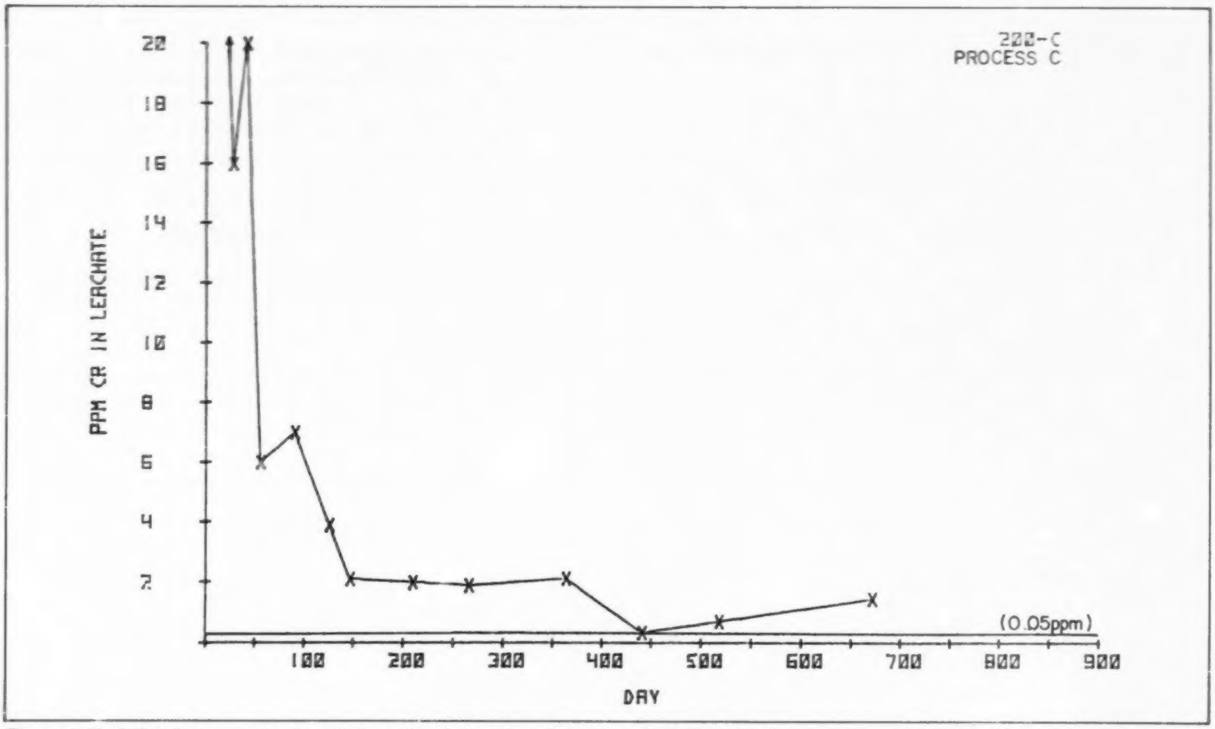

Figure 6. Variation in concentration of chromium in leachate from process C fixed sludge with time. Horizontal line at 0.05 ppm indicates public water supply standard.

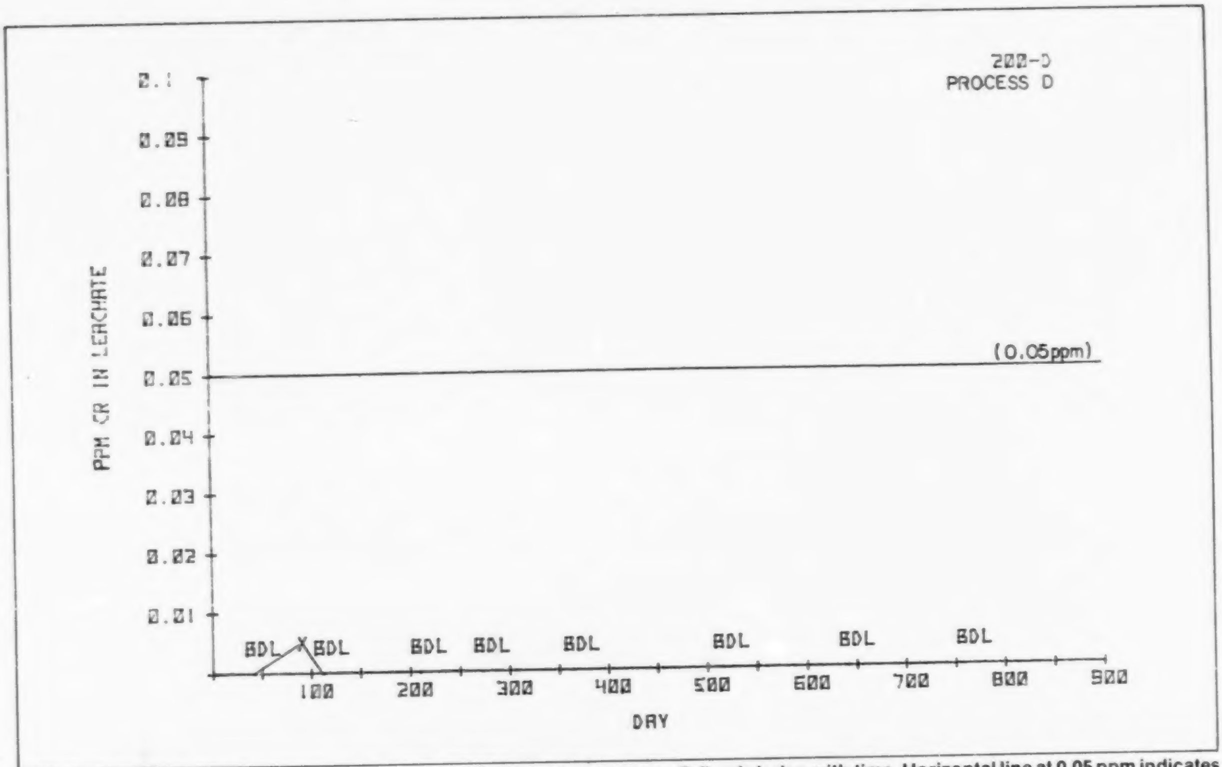

Figure 7. Variation in concentration of chromium in leachate from process D fixed sludge with time. Horizontal line at 0.05 ppm indicates public water supply standard.

CONCLUSIONS AND RECOMMENDATIONS

Of the four hazardous sludge fixation systems examined, the encapsulation system is the most effective in containing potential pollutants in electroplating wastes. Systems using an additive only, with no encapsulation, showed a wide range of efficiencies in containment; but, none showed the overall effectiveness of encapsulation.

Significant reductions in fixation efficiency were noted in additive systems that required the acidification of the electroplating waste. Fixation processes that resulted in increased permeability in the fixed sludge (Processes B and C) produced samples that leached larger amounts of pollutants than those that decreased permeability (Processes A and D).

The elutriate or shake test results were confirmed by the long-duration column leaching test. The shake test is a useful system for evaluating the performance of fixation processes.

On the basis of this investigation, the following recommendations can be made:

a) Additional work should be undertaken on developing encapsulation systems. Reductions in cost and an increase in the proportion of waste that can be encapsulated would make this disposal system attractive to potential users.

b) The additive-only processes tested should be used on electroplating wastes only in cases where strict control and monitoring of the landfill is possible.

c) Field studies of landfill sites where fixed sludges have been placed would be a useful step in confirming the safety or lack of safety involved in fixed sludge disposal.

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